unit

8

Chemical Equilibrium Focusing on Acid–Base Systems

Equilibrium describes any condition or situation of balance. We recognize equilibrium in a chemical reaction system, oddly enough, by noticing nothing—we see no change in any property of the system. The easiest conclusion to draw would be that nothing is happening, but closer study reveals that, at the molecular level, a lot of change is going on.

Chemical reaction equilibrium is always a *dynamic balance* between two *opposing* changes, which are balanced because they are occurring at *equal* rates, within a *closed* system. What we observe directly is the net effect—neither an increase nor a decrease in any measurable property.

Chemistry involves the study of change in chemical substances. To predict and control chemical change, we must better understand the nature of the system at the molecular level. For instance, to understand why and how bubbles of gas form or dissolve in a liquid, we must take into account the nature of the gas, the nature of the liquid, and the actions of their invisible entities—all at the same time.

This unit explores the nature of dynamic equilibrium in chemical systems. It explains much more thoroughly and completely many of the chemical change concepts you have already learned. You will examine some very important reactions—those involving acids and bases in solution—at a higher conceptual level. This knowledge will allow you to describe, explain, and predict many new chemical systems and situations. The continual exploration and improvement of concepts such as these is a critical part of the nature of science.

As you progress through the unit, think about these focusing questions:

- What is happening in a system at equilibrium?
- How do scientists predict shifts in the equilibrium position of a system?
- How do Brønsted–Lowry acids and bases illustrate equilibrium?

GENERAL OUTCOMES

In this unit, you will

- explain that there is a dynamic balance of opposing reactions in chemical systems at equilibrium
- determine quantitative relationships in acid–base ionization and other simple systems at equilibrium

Unit 8
Chemical Equilibrium Focusing on Acid–Base Systems

ARE YOU READY?

These questions will help you find out what you already know, and what you need to review, before you continue with this unit.

Prerequisites

Concepts

- collision–reaction theory
- dissociation and ionization
- amount concentration
- ion concentration
- percent reaction
- stoichiometric calculation
- net ionic equations
- acids and bases
- indicators

Skills

- laboratory safety
- scientific problem solving

You can review prerequisite concepts and skills in the appendices and on the Nelson Web site.

A Unit Pre-Test is also available online.

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Knowledge

1. A large number of chemical reactions (most notably redox reactions) will *only* occur in aqueous solution, at least at a rate great enough to be observable in a laboratory. In terms of collision–reaction theory (**Figure 1**), state
   (a) why a given reaction might only occur in solution
   (b) why collisions between entities do not necessarily result in reaction
   (c) the two effects that an increase in temperature has on collisions between entities involved in a reaction
   (d) the effect that an increase in concentration of one kind of entity has on collisions between all entities involved in a reaction

An Ineffective Collision

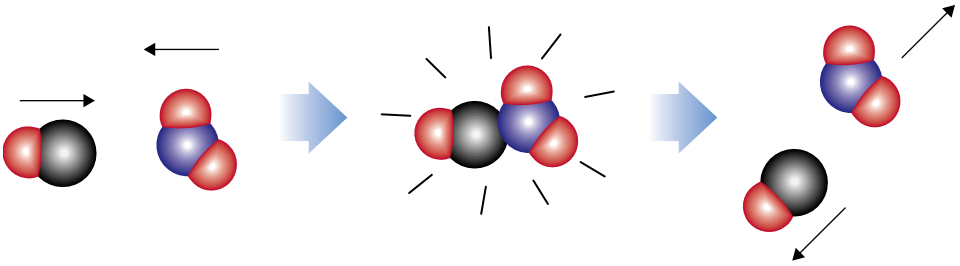

Figure 1
Collision–reaction theory considers the numbers, speeds, and orientation of colliding entities to explain the progress of chemical reactions.

2. Assume that each of the following substances is placed in water. Rewrite the formula and the physical state to indicate whether it is very soluble or only slightly soluble in water at SATP. For those substances predicted to produce ions in solution, write symbols for all aqueous ions present after the substance dissociates upon dissolving.
   (a) $MgSO_4 \cdot 7H_2O(s)$
   (b) $CH_3COCH_3(l)$
   (c) $CH_2CH_2(g)$
   (d) $CaCO_3(s)$
   (e) $PbCl_2(s)$
   (f) $FeCl_3(s)$
   (g) $C_3H_5(OH)_3(l)$

3. Each of the following substances is mixed with water to form an aqueous solution. Write an equation (using the modified Arrhenius theory) to explain the acidity or basicity of the solution in terms of hydronium or hydroxide ions. Your equations should, when necessary, represent the "ionizing" of the substance as a reaction with water.
   (a) $HCl(g)$
   (b) $CH_3COOH(l)$
   (c) $H_2SO_4(l)$
   (d) $HNO_3(l)$
   (e) $NaCl(s)$
   (f) $NH_3(g)$
   (g) $NaOH(s)$

4. The concentration of chemical substances in solution can vary widely (**Figure 2**). Concentration affects solution properties such as colour, conductivity, freezing point, and viscosity. Concentration also affects the frequency of particle (entity) collisions; and, thus, will usually affect the observed rate of a reaction. Complete **Table 1**.

Table 1 Concentration of Entities and Quantities of Reagents in Solution

Reagent	Mass dissolved (g)	Solution volume (L)	Entity	Amount Concentration (mol/L)
NaOH(s)	1.74	0.500	$OH^-(aq)$	
$Al_2(SO_4)_3(s)$		2.00	$SO_4^{2-}(aq)$	0.100
$Al_2(SO_4)_3(s)$		2.00	$Al^{3+}(aq)$	0.100
$CaCl_2(s)$	1.00		$Cl^-(aq)$	0.00440

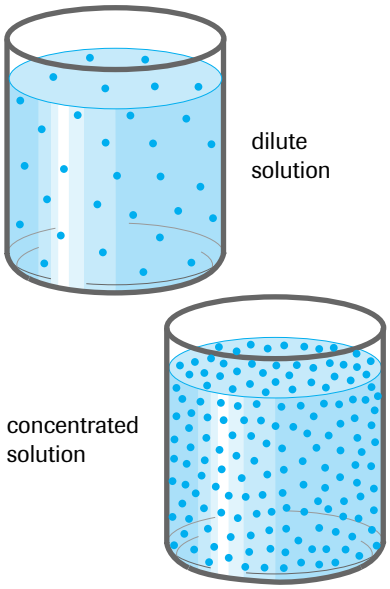

Figure 2
Concentration affects the rate of chemical reaction as well as physical properties.

5. Chemical substances may also have widely varying concentrations in the gaseous state. Calculate the amount concentration of
   (a) 24.0 g of hydrogen in a 2.00 L container
   (b) 500 kPa of oxygen in a 10.0 L container at 0 °C
   (c) 4.40 mol of carbon dioxide at SATP
   (d) 0.227 mol of methane at STP

6. Understanding chemical equilibrium theory often involves using a net ionic equation. For each of the following combinations of reagents, predict the product(s), and write a net ionic reaction equation. Balance the equation with simplest integer coefficients, and include physical states for all substances.
   (a) Copper(II) chloride and potassium carbonate solutions are mixed.
   (b) Ethene (ethylene) reacts with hydrogen chloride to form chloroethane.
   (c) Aluminium foil reacts with hydrochloric acid.
   (d) Ammonia undergoes simple decomposition.
   (e) Magnesium metal is placed in an aqueous solution of gold(III) chloride.
   (f) Mixing sulfurous acid solution with sodium hypochlorite solution results in a spontaneous redox reaction.

7. The acidity of solutions often has a considerable effect on the type, rate, and extent of the reactions they will undergo. Acids may be classed as strong or weak, depending on the extent of their reaction with water. Complete **Table 2**, identifying the acids as strong or weak.

Table 2 Solution Acidity and Basicity

Acid	Strength S/W	[Acid] (mol/L)	% Reaction in/with water	pH	$[H_3O^+(aq)]$ (mol/L)
HCl(aq)		0.016	>99		
HBr(aq)			>99		0.024
$HNO_3(aq)$			>99	4.0	
$CH_3COOH(aq)$		0.100	1.3		
HCN(aq)		0.200		5.0	
$HNO_2(aq)$		0.010	7.0		

chapter

15 Equilibrium Systems

In this chapter

- Exploration: Shakin' the Blues
- Investigation 15.1: The Extent of a Chemical Reaction
- Web Activity: Equilibrium State
- Mini Investigation: Modelling Dynamic Equilibrium
- Lab Exercise 15.A: The Synthesis of an Equilibrium Law
- Web Activity: Paul Kebarle
- Lab Exercise 15.B: Determining an Equilibrium Constant
- Web Activity: Writing Equilibrium Expressions
- Investigation 15.2: Equilibrium Shifts (Demonstration)
- Biology Connection: CO_2 Transport
- Investigation 15.3: Testing Le Châtelier's Principle
- Case Study: Urea Production in Alberta
- Lab Exercise 15.C: The Nitrogen Dioxide–Dinitrogen Tetraoxide Equilibrium
- Investigation 15.4: Studying a Chemical Equilibrium System
- Web Activity: Poison Afloat

Equilibrium in Chemical Systems

The simplest equilibrium systems are *static*. Nothing is moving or changing to create the balance. A textbook sitting on a level desktop is an example of *static equilibrium*. It stays motionless because two equal and opposite forces act on it simultaneously. The downward pull of Earth (gravity) on the book is exactly balanced by the upward push by the desktop. A laboratory balance is a common technology that uses this kind of equilibrium.

Chemical equilibrium is also a balance between two opposing agents of change, but always in a *dynamic* system. An expert juggler in performance (**Figure 1**) is similar to a chemical system at equilibrium. The juggler's act is a *dynamic equilibrium*, with some balls moving upward and some moving downward at any given moment. There is no net change because the rates of upward movement and downward movement are equal at any given moment.

Chemical systems at equilibrium have constant observable properties. Nothing appears to be happening because the internal movement involves entities that are too small to see. A critical task of chemical engineers is to disturb (unbalance) chemical equilibria in industrial reactions. Production of specific desired products is controlled by manipulating the conditions under which reactions occur. Some general concepts apply to all chemical equilibrium systems; these concepts are the focus of this chapter.

STARTING Points

Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.

1. What, precisely, is happening to the chemical entities involved in a reaction while observation shows that products are being formed?
2. Is anything happening to the chemical entities involved in a reaction when observation shows the reaction appears to have stopped, with no more products being formed?
3. Why do some reactions seem to occur partially, and apparently stop while some of all of the reactants are still present, while in other reactions all of the limiting reagent appears to be consumed?
4. Can the chemical amount of product be predicted successfully for reactions that are not quantitative?

Career Connection:
Food Science Technologist; Chemical Process Engineer

Figure 1
How is a juggler similar to a chemical system in equilibrium?

Exploration — Shakin' the Blues

When small pieces of zinc are added to a dilute solution of excess hydrochloric acid in an open beaker (**Figure 2**), a vigorous reaction occurs with lots of gas and heat given off. The zinc continues to react and, when it is completely consumed, the visible signs of reaction come to an end. After seeing many reactions such as this one in your science studies, you may have come to think that all chemical reactions only go one way: from reactants to products. But do they always?

Materials: lab apron; eye protection; 400 mL flask and stopper; 250 mL water; 5.0 g potassium hydroxide (KOH(s)); 3.0 g glucose or dextrose; 2% methylene blue; stirring rod

- Pour 250 mL of water into the flask.
- Add 6 drops of methylene blue and all of the potassium hydroxide and glucose to the flask.
- Stir the mixture with the stirring rod until the solids have dissolved.
- Stopper the flask and set it on the bench. Observe the colour of the solution.
- Shake the solution vigorously and note any changes (**Figure 3**).
- Set the flask on the table and leave it standing until another change is noticed.
- Repeat the previous two steps many times. Make observations each time.

(a) Describe the reaction in the flask in relation to the discussion at the beginning of this activity.

(b) What evidence do you have to substantiate your answer to question (a)?

(c) Predict whether the colour changes will continue forever.

- Test your prediction over a reasonable period of time.

(d) Evaluate your prediction.

Potassium hydroxide is poisonous and corrosive.

Keep potassium hydroxide away from skin and eyes. Wear eye protection.

Figure 2
Zinc reacts rapidly and quantitatively with hydrochloric acid.

Figure 3
How many times does this reaction happen?

15.1 Explaining Equilibrium Systems

Figure 1
When the pressure on this equilibrium system changes, the equilibrium is disturbed.

Scientists describe chemical systems in terms of empirical properties such as temperature, pressure, volume, and amounts of substances present. Chemical systems are simpler to study when separated from their surroundings by a definite boundary. This separation gives an experimenter control over the system so that no matter can enter or leave. Such a physical arrangement is called a **closed system**. A reaction in solution in a test tube or a beaker can be considered a closed system, as long as no gas is used or produced in the reaction. Systems involving gases must be closed on all sides by a solid container. Separating a chemical reaction system from its surroundings makes studying its properties, conditions, and changes much simpler. The use of controlled systems is an integral part of scientific study.

Closed Systems at Equilibrium

One example of a chemical system at equilibrium is a soft drink in a closed bottle—a closed system in equilibrium. Nothing appears to change, until the bottle is opened. Removing the bottle cap and reducing the pressure alters the equilibrium state, as the carbon dioxide is allowed to leave the system (**Figure 1**). Carbonated drinks that have gone "flat" because of the decomposition of carbonic acid can be carbonated again by the addition of pressurized carbon dioxide to the solution to reverse the reaction, and then capping the container to restore the original equilibrium.

Collision–reaction theory is fundamental to the study of chemical systems. As originally introduced in this textbook to provide a basis for stoichiometric calculations, this theory required us to initially assume, for simplicity, that reactions are always spontaneous, rapid, quantitative, and stoichiometric. Common experience, however, shows that this assumption is not always true. Not all reactions are rapid; for example, corrosion of a car body may take years. A study of oxidation–reduction reactions soon provides evidence that many reactions are not spontaneous. This chapter will examine and test the assumption of quantitative reaction in detail to significantly increase your understanding of chemical systems.

INVESTIGATION 15.1 *Introduction*

The Extent of a Chemical Reaction

In Chapter 8, you performed experiments that produced evidence that reactions are quantitative. In a quantitative reaction, the limiting reagent is completely consumed. To identify the limiting reagent, you can test the final reaction mixture for the presence of the original reactants. For example, in a diagnostic test, you might try to precipitate ions from the final reaction mixture that were present in the original reactants.

Purpose

The purpose of this investigation is to test the validity of the assumption that chemical reactions are quantitative.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (1, 2, 3)
○ Hypothesis	● Procedure	
● Prediction	● Evidence	

Problem

What are the limiting and excess reagents in the chemical reaction of selected quantities of aqueous sodium sulfate and aqueous calcium chloride?

Design

Samples of sodium sulfate solution and calcium chloride solution are mixed in different proportions and the final mixture is filtered. Samples of the filtrate are tested for the presence of excess reagents, using diagnostic tests.

To perform this investigation, turn to page 700.

Practice

1. The evidence gathered in Investigation 15.1 may be classified as an anomaly—an unexpected result that contradicts previous rules or experience.
   (a) Write the balanced equation for the double replacement reaction of sodium sulfate and calcium chloride solutions.
   (b) Write a statement describing the anomaly that occurred, using chemical names from the equation.
   (c) Write the net ionic equation for the reaction.
   (d) Use chemical names from the net ionic equation to write a statement about the anomaly.
   (e) Which of the previous statements more accurately describes the chemical system, according to collision–reaction theory?
2. When scientists first encounter an apparent anomaly, they carefully evaluate the design, procedure, and technological skills involved in an investigation. One important consideration is the reproducibility of the evidence. Compare your evidence in Investigation 15.1 with the evidence collected by other groups. Is there support for the reproducibility of this evidence?

Evidence obtained from many reactions contradicts the assumption that reactions are always quantitative. In Investigation 15.1, there is direct evidence for the presence of both reactants after the reaction appears to have stopped. This apparent anomaly can be explained, in terms of collision–reaction theory, by the idea that a reverse reaction can occur: the products, calcium sulfate and sodium chloride, can react to re-form the original reactants. The final state of this chemical system can be explained as a competition between collisions of reactants to form products and collisions of products to re-form reactants.

$$Na_2SO_4(aq) + CaCl_2(aq) \underset{\text{reverse}}{\overset{\text{forward}}{\rightleftarrows}} CaSO_4(s) + 2\,NaCl(aq)$$

This competition requires that the system be closed so that reactants and products cannot escape from the reaction container. The chemical system in Investigation 15.1 can be considered a closed system, bounded by the volume of the liquid phase.

We assume that any closed chemical system with constant macroscopic properties (no observable change occurring) is in a state of **equilibrium**, usually classified, for convenience, as one of three types. **Phase equilibrium** involves a single chemical substance existing in more than one phase in a closed system. Water placed in a sealed container evaporates until the water vapour pressure (concentration of water in the gas phase) rises to a maximum value, and then remains constant (**Figure 2**). **Solubility equilibrium** involves a single chemical solute interacting with a solvent substance, where excess solute is in contact with the saturated solution (**Figure 3**). A **chemical reaction equilibrium** involves several substances: the reactants and products of a chemical reaction. All three types of equilibrium are explained by a theory of **dynamic equilibrium**—a balance between two opposite processes occurring at the same rate.

The terms *forward* and *reverse* are used to identify which process is being referred to, and are specific to a written equilibrium equation. When any equation is written with arrows to show that the change occurs both ways, the left-to-right change is called the **forward reaction**, and the right-to-left change is called the **reverse reaction**.

DID YOU KNOW ?

Anomalies—Signals for Change

Anomalies, or discrepant events, are important as scientists acquire and develop scientific knowledge. Sometimes these events have been ignored, discredited, or elaborately explained away by scientists who do not wish to question or reconsider accepted laws and theories. Investigating anomalies sometimes leads to the restriction, revision, or replacement of scientific laws and theories.

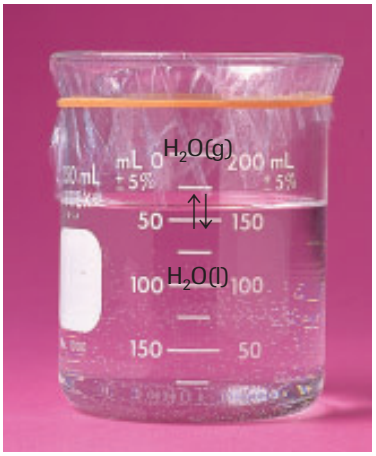

Figure 2
According to the theory of dynamic equilibrium, as long as the container remains closed at constant temperature, the rate at which molecules in the liquid state evaporate is equal to the rate at which molecules in the gas state condense.

$$H_2O(l) \rightleftarrows H_2O(g)$$

Figure 3
For excess solid copper(II) sulfate in equilibrium with its saturated aqueous solution, the rates of dissolving and crystallization are equal.

$$CuSO_4(s) \rightleftarrows Cu^{2+}(aq) + SO_4^{2-}(aq)$$

WEB Activity

Simulation—Equilibrium State

This simulation illustrates the establishment of a simple dynamic equilibrium by showing how the concentrations of entities change over time, beginning from an initial condition. A textbook can only represent this process as a sequence of static (still) diagrams (such as those in **Figure 4**) or graphs (such as that in **Figure 5**).

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mini Investigation Modelling Dynamic Equilibrium

This activity models the progress of a chemical reaction to equilibrium, representing concentrations of reactants and products as volumes of water. The establishment of equilibrium is graphed as volume versus number of transfers. This graph then represents a typical concentration–time graph of a chemical reaction to equilibrium.

Materials: two drinking straws of different diameters; two 25 mL graduated cylinders; graph paper; water; meniscus finder

- Label one 25 mL graduated cylinder **R** (for reactants), and fill with water to the 25.0 mL mark.
- Label the other cylinder **P** (for products) and leave it empty.
- Holding a straw in each hand, place one straw in each graduated cylinder so that each straw rests on the bottom of its cylinder. Use the larger straw in the **R** cylinder.
- Transfer water simultaneously from each cylinder to the other by placing an index finger over the open end of each straw (to seal it). Then lift the straws out of their original cylinders, move the bottom of each straw over the *other* cylinder, and lift your index fingers to allow the water in each straw to drain into the cylinder below. Replace the straws in their original cylinders.
- After each transfer, measure and record the volume of water in each cylinder to 0.1 mL. Also record the number of the transfer.
- Repeat the transfer step until no significant change in water volumes has occurred for at least three transfers.
- Graph the volume of water in each cylinder as a dependent (responding) variable against the number of transfers as the independent (manipulated) variable.
- Repeat the activity, switching the straws used in each cylinder. Plot the values on the same axes as for the first trial.

(a) How does the graph change, and how is it the same, when the smaller straw is initially in the **R** cylinder?

(b) How would doing the transfers more slowly affect the final volumes in each cylinder?

(c) How would replacing the larger straw with an even larger one affect the final volumes in each cylinder?

(d) Express the equilibria of the water transfer trials as percent yields; that is, the percentage of "reactant" water that is converted to "product".

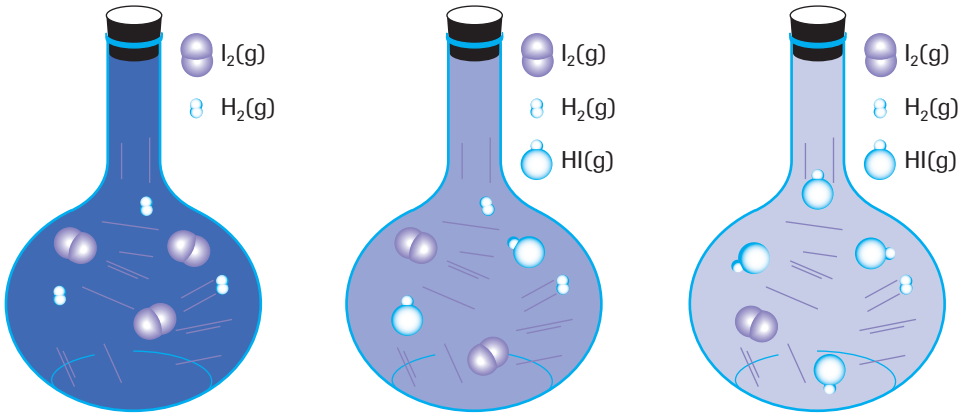
(e) Predict the graph's shape if both of the straws chosen had the same diameter.

Chemical Reaction Equilibrium

Chemical reaction equilibria are more complex than phase or solubility equilibria, due to the variety of possible chemical reactions and the greater number of substances involved. To explain chemical equilibrium systems, we need to combine ideas from atomic theory, kinetic molecular theory, collision–reaction theory, and the concepts of reversibility and dynamic equilibrium. Although this synthesis is successful as a description, and also as an explanation, it has only limited application in predicting quantitative properties of an equilibrium system.

The Hydrogen–Iodine Reaction System

Chemists have studied the reaction of hydrogen gas and iodine gas extensively, because the molecules are simple in structure and the reaction takes place in the gas phase. Once hydrogen and iodine are mixed, the reaction proceeds rapidly at first. The initial dark purple colour of the iodine vapour gradually fades, and then remains constant (**Figure 4**).



Initially, hydrogen (in excess) and iodine are added to the flask. The colour of the iodine vapour is the only easily observable property.

Early in the reaction, hydrogen and iodine form hydrogen iodide faster than hydrogen iodide forms hydrogen and iodine. Overall, the amount of iodine decreases, so the colour of the flask contents appears to lighten. Both hydrogen and hydrogen iodide are colourless.

At equilibrium, analysis shows that the flask contains all three substances. The purple colour shows that some iodine remains. The constancy of the colour is evidence that equilibrium exists. Forward and reverse reactions are occurring at equal rates.

Figure 4
When hydrogen and iodine are added to the flask, the colour of the iodine vapour is the only easily observable (empirical) property. An equilibrium equation describes this evidence theoretically.
$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$, $t = 448$ °C

Table 1 contains data from three experiments with the hydrogen–iodine system: one in which hydrogen and iodine are mixed; one in which hydrogen, iodine, and hydrogen iodide are mixed; and one in which only hydrogen iodide is present initially. At a temperature of 448 °C, the system quickly reaches an observable equilibrium each time. Chemists use evidence such as that in Table 1 to describe a state of equilibrium in two ways: in terms of percent reaction and in terms of an equilibrium constant. Percent reaction describes the equilibrium for one specific system example only, whereas an equilibrium constant describes all systems of the same reaction at a given temperature. Alternatively, you can draw a graph of the reaction progress, plotting quantity (or concentration) of the reagents versus time (**Figure 5**).

Table 1 The Hydrogen–Iodine System at 448 °C

System	Initial system concentrations (mmol/L)			Equilibrium system concentrations (mmol/L)		
	$H_2(g)$	$I_2(g)$	HI(g)	$H_2(g)$	$I_2(g)$	HI(g)
1	5.00	5.00	0	1.10	1.10	7.80
2	0.50	0.50	1.70	0.30	0.30	2.10
3	0	0	3.20	0.35	0.35	2.5

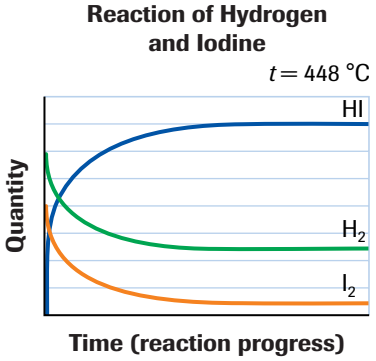


Figure 5
The graph of the quantity of each substance against time shows that the rate of reaction of the reactants decreases as the number of reactant molecules decreases, and the rate at which the product changes back to reactants increases as the number of product molecules increases. These two rates must become equal at some point, after which the quantity of each substance present will not change.

DID YOU KNOW ?

Lavoisier and Closed Systems

Antoine Laurent Lavoisier (1743–1794) is recognized as the father of modern chemistry for many reasons. He created the basic nomenclature system we still use for compounds, demonstrated the law of conservation of mass, and explained and clarified the theory of combustion. Most importantly, perhaps, his successes convinced the chemical community of the critical importance of his methods of careful measurement, and of carrying out experiments in closed systems—carefully accounting for, and preventing, invisible reactants and products (notably, gases) from escaping. When chemists began to understand the importance of maintaining closed systems in order to draw correct conclusions about reactions, chemistry could finally move forward as a true science.

Learning Tip

When a reaction is shown to be quantitative (as written in the equation), it means that the reverse reaction happens so little that it can be ignored for all normal purposes. Another way to think of a quantitative reaction is that if the products shown (as written) were mixed together as reactants, there would be no apparent reaction. A reaction that is quantitative in the forward direction is necessarily nonspontaneous in the reverse direction. In this unit, we will (arbitrarily) assume that "quantitative" specifies a reaction that, at equilibrium, is more than 99.9% complete. Another way to think of it is that less than one part per thousand (0.1%) of an original reactant remains unreacted, at equilibrium, in a quantitative reaction.

A percent yield is defined as the yield of product measured at equilibrium compared with the maximum possible yield of product. In other words, percent yield can be useful for communicating the *position of an equilibrium*. The maximum possible yield of product is calculated using the method of stoichiometry, assuming a quantitative forward reaction with no reverse reaction. Percent yield provides an easily understood way to refer to quantities of chemicals present in equilibrium systems. For example, analysis of the evidence in System 1, Table 1, shows that, at 448 °C, this particular hydrogen–iodine system reaches an equilibrium with a percent yield of 78.0% (**Table 2**).

Table 2 Percent Yield of the Hydrogen–Iodine System at 448 °C

System	Equilibrium [HI]* (mmol/L)	Maximum possible [HI]* (mmol/L)	Percent yield (%)
1	7.80	10.0	78.0
2	2.10	2.70	77.8
3	2.50	3.20	78.1

*Square brackets [ ] indicate amount concentration.

Equilibrium arrows ($\rightleftarrows$) communicate that an equilibrium exists. To communicate the extent of a reaction, a percent yield may be written above the equilibrium arrows in a chemical equation. The following equation describes the position of a hydrogen–iodine equilibrium in System 1, Table 2, at 448 °C.

$$H_2(g) + I_2(g) \overset{78\%}{\rightleftarrows} 2\,HI(g) \qquad t = 448\ °C$$

Scientists now think of all chemical reactions as occurring in both forward and reverse directions. Any reaction falls loosely into one of four categories. Reactions that favour reactants very strongly, that is, reactions that normally have a percent yield of much less than 1%, are simply observed as being nonspontaneous. In these reactions, mixing reactants has no observable result. Reactions producing observable equilibrium conditions may react less or more than 50%, favouring reactants or products respectively. Significant amounts of both reactants and products are always present. Finally, reactions that favour products very strongly, much more than 99%, are observed to be complete (*quantitative*). The chemical equations for quantitative reactions are generally written with a single arrow to indicate that the effect of the reverse reaction is negligible. **Table 3** shows how percent yield may be used to classify equilibrium systems and how the classification may be communicated in reaction equations.

Table 3 Classes of Chemical Reaction Equilibria

Percent yield	Description of equilibrium	Position of equilibrium
negligible	nonspontaneous (no apparent reaction)	
$< 50\%$	reactants favoured	$< 50\% \rightleftarrows$
$> 50\%$	products favoured	$> 50\% \rightleftarrows$
$> 99.9\%$	quantitative	$\rightarrow$

When considering equilibrium systems, we cannot use the simple assumption of quantitative reaction. When there is no limiting reagent for a reaction, and when we cannot assume complete reaction, stoichiometric calculations require a little more thought. Such calculations may conveniently be set up as an **ICE table**, meaning that the *initial*, *change*, and *equilibrium* values are arranged in tabular form.

SAMPLE problem 15.1

Consider the reaction equation for the formation of hydrogen iodide at 448 °C. Assume the reaction is begun with 1.00 mmol/L concentrations of both $H_2(g)$ and $I_2(g)$. Construct an ICE table to determine equilibrium concentrations of the reagents. The equilibrium concentration of $I_2(g)$ (determined by colour intensity) is 0.22 mmol/L.

Set up the ICE table as follows:

Table 4 The $H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$ Equilibrium

Concentration	$[H_2(g)]$ (mmol/L)	$[I_2(g)]$ (mmol/L)	$[HI(g)]$ (mmol/L)
Initial	1.00	1.00	0.00
Change			
Equilibrium		0.22	

Begin by calculating the change (*decrease*) in concentration of iodine.

$(0.22 - 1.00)$ mmol/L $= -0.78$ mmol/L

The changes of the other concentrations may be calculated directly from this value, using stoichiometric ratios from the balanced equation.

For hydrogen, the change is also a *decrease* (negative value) of

$$0.78 \text{ mmol/L} \times \frac{1}{1} = -0.78 \text{ mmol/L}$$

For hydrogen iodide, the change is an *increase* (positive value) of

$$0.78 \text{ mmol/L} \times \frac{2}{1} = +1.6 \text{ mmol/L}$$

Complete the ICE table, using these values to enter the concentrations at equilibrium.

Table 5 The $H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$ Equilibrium

Concentration	$[H_2(g)]$ (mmol/L)	$[I_2(g)]$ (mmol/L)	$[HI(g)]$ (mmol/L)
Initial	1.00	1.00	0.00
Change	−0.78	−0.78	+1.6
Equilibrium	0.22	0.22	1.6

In Sample Problem 15.1, notice that *every* substance in the reaction is a gas. Therefore, all of the stoichiometric calculations can use concentrations directly, rather than chemical amounts, because the volume must be the same for every gaseous substance in a closed container. The volume is a common factor in the calculation step that uses the stoichiometric ratio. This same reasoning means that concentrations can also be used directly for stoichiometric calculation whenever every substance in a reaction is an aqueous entity dissolved in the same volume of solvent.

DID YOU KNOW?

Diabetes: Blood Sugar Equilibrium

For people with diabetes, reaction equilibrium established by sugar in the human body is critically important. Recent advances in the technology allow testing of blood sugar concentration with personal devices such as the One Touch® SureStep® blood-glucose meter (**Figure 6**). The meter displays the concentration in mmol/L after analyzing a single drop of blood extracted from a fingertip. Multiple readings, including date and time, are stored electronically and can be displayed at any time. The data can be downloaded to a computer.

Figure 6
This device helps diabetics monitor their blood glucose levels.

CAREER CONNECTION

Food Science Technologist

The development and analysis of food products for individuals with diabetes is crucial. Food science technologists carefully measure and conduct tests on carbohydrates so that patients can control their blood sugar equilibrium.

Learn more about the many food industries that employ food science specialists.

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Practice

3. For a chemical system at equilibrium:
(a) What are the observable characteristics?
(b) Why is the equilibrium considered "dynamic"?
(c) What is considered "equal" about the system?

4. In a gaseous reaction system, 2.00 mol of methane, $CH_4(g)$, is initially added to 10.00 mol of chlorine, $Cl_2(g)$. At equilibrium the system contains 1.40 mol of chloromethane, $CH_3Cl(g)$, and some hydrogen chloride, $HCl(g)$.
(a) Write a balanced reaction equation for this equilibrium and calculate the maximum possible yield of chloromethane product.
(b) Calculate the percent yield at this equilibrium and state whether products or reactants are favoured.

5. Combustion reactions, such as the burning of methane, often favour products so strongly that they are written with a single arrow. Assuming the forward reaction has a very low activation energy (Chapter 12) and the reverse reaction has a very high activation energy (to account for the difference in the tendency to occur), sketch a possible potential energy diagram representing the progress of such a reaction.

6. After 4.0 mol of $C_2H_4(g)$ and 2.50 mol of $Br_2(g)$ are placed in a sealed container, the reaction

$$C_2H_4(g) + Br_2(g) \rightleftarrows C_2H_4Br_2(g)$$

establishes an equilibrium. **Figure 7** shows the concentration of $C_2H_4(g)$ as it changes over time at a fixed high temperature until equilibrium is reached.

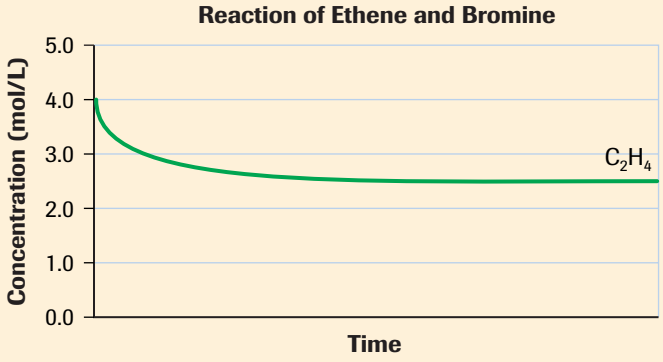

Figure 7
A graph of the reaction of ethene with bromine

(a) Sketch this graph. Draw lines on your copy to show how the concentration of each of the other two substances changes.
(b) Create an ICE table, using reagent amount concentrations.
(c) What is the volume of the container?
(d) Calculate the percent yield of dibromoethane.

7. Write a balanced net ionic equation for each of the following described reactions, showing appropriate use of equilibrium "arrow" symbols where appropriate, and indicating (with symbols) whether products or reactants are favoured.
(a) An excess of solid copper reacts with virtually all of the silver ions in a sample solution.
(b) When a solution containing calcium ions is mixed with a solution containing a large excess of sulfate ions, a precipitate forms, but tests indicate that a small quantity of calcium ions remains in solution.
(c) When acetic acid is dissolved in water, the acetic acid molecules react with water molecules to form hydronium and acetate ions. Careful pH testing shows that about 980 of every 1000 acetic acid molecules remain in their molecular form, at equilibrium.

Learning Tip

Chemists often refer to "homogeneous" reaction systems. This term means that every entity involved in the reaction exists in the same physical state. The reaction from Sample Problem 15.1, where all reactants and products are gases, is a typical case. The other common case involves reactions where all entities involved are in aqueous solution. A system that has more than one phase, such as solid copper reacting in aqueous silver nitrate solution, is a "heterogeneous" reaction system.

LAB EXERCISE 15.A

The Synthesis of an Equilibrium Law

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ○ Evidence
- ● Analysis
- ○ Evaluation

The following chemical equation represents a chemical equilibrium:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{2+}(aq)$$

This equilibrium is convenient to study because the colour of the system characterizes the equilibrium position of the system (**Figure 8**).

Purpose

The purpose of this investigation is the synthesis of an equilibrium law.

Problem

What mathematical formula, using equilibrium concentrations of reactants and products, gives a constant for the iron(III)–thiocyanate reaction system?

Figure 8
The two reactants combine to form a dark red equilibrium mixture. The red colour of the solution is due to the aqueous thiocyanate–iron(III) product, $FeSCN^{2+}(aq)$.

Design

Reactions are performed using various initial concentrations of iron(III) nitrate and potassium thiocyanate solutions. The equilibrium concentrations of the reactants and the product are determined from the measurement and analysis of the colour intensity using a spectrophotometer. Possible mathematical relationships among the concentrations are tried and analyzed to determine if the mathematical formula gives a constant value.

Evidence

Table 6 Iron(III)–Thiocyanate Equilibrium at SATP

Trial	$[Fe^{3+}(aq)]$ (mol/L)	$[SCN^{-}(aq)]$ (mol/L)	$[FeSCN^{2+}(aq)]$ (mol/L)
1	3.91×10^{-2}	8.02×10^{-5}	9.22×10^{-4}
2	1.48×10^{-2}	1.91×10^{-4}	8.28×10^{-4}
3	6.27×10^{-3}	3.65×10^{-4}	6.58×10^{-4}
4	2.14×10^{-3}	5.41×10^{-4}	3.55×10^{-4}
5	1.78×10^{-3}	6.13×10^{-4}	3.23×10^{-4}

Analysis

Test the following mathematical relationships for constancy:

1. $[Fe^{3+}(aq)][SCN^{-}(aq)][FeSCN^{2+}(aq)]$
2. $[Fe^{3+}(aq)] + [SCN^{-}(aq)] + [FeSCN^{2+}(aq)]$
3. $\dfrac{[FeSCN^{2+}(aq)]}{[Fe^{3+}(aq)][SCN^{-}(aq)]}$
4. $\dfrac{[Fe^{3+}(aq)]}{[FeSCN^{2+}(aq)]}$
5. $\dfrac{[SCN^{-}(aq)]}{[FeSCN^{2+}(aq)]}$

WWW *WEB Activity*

Canadian Achievers—Paul Kebarle

Paul Kebarle (**Figure 9**) pioneered the measurements of gas-phase ion-molecule equilibria. Kebarle's findings, now significantly expanded by other workers, constitute a central database that is of fundamental importance in many diverse fields of scientific research.

1. What fundamental data did Kebarle and his co-workers obtain from their research?
2. List three fields of research that Kebarle's work has aided.

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Figure 9
Paul Kebarle

DID YOU KNOW ?

Computers

Scientists often use computers to analyze numerical evidence in order to establish mathematical relationships among experimental variables. The mathematical formulas derived are useful in understanding chemical processes and in applying these processes to technology.

DID YOU KNOW ?

Related Interests

Two Norwegian chemists, Cato Maximilian Guldberg and Peter Waage, conducted detailed empirical studies of many equilibrium systems in the mid-1800s (**Figure 10**). By 1864, they had proposed a mathematical description of the equilibrium condition that they called the "law of mass action." Analyzing the results of their experiments, Guldberg and Waage noticed that, when they arranged the equilibrium concentrations into a specific form of ratio, the resulting value was the same no matter what combinations of initial concentrations were mixed.

Figure 10
Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900) were related by more than their interest in chemistry: They were brothers-in-law!

Learning Tip

It is common practice (convention) to ignore units and list only the numerical value for an (amount concentration) equilibrium constant. The expression of units is often very complex for K_c relationships. But, because each entity concentration is always entered with mol/L units, any entity concentration we calculate from a K_c value will always give an answer having mol/L units, so you need only memorize this (simplifying) rule.

The Equilibrium Constant, K_c

Analysis of the evidence from many experiments such as those in Lab Exercise 15.A (page 683) reveals a mathematical relationship that provides a constant value for a chemical system over a range of amount concentrations. This constant value is called the **equilibrium constant**, K_c, for the reaction system. Evidence and analysis of many equilibrium systems have resulted in the following **equilibrium law**.

For the reaction $a\,A + b\,B \rightleftarrows c\,C + d\,D$,

the equilibrium law expression is $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

In this mathematical expression, A, B, C, and D represent chemical entity formulas and a, b, c, and d represent their coefficients in the balanced chemical equation. The relationship holds *only* when amount concentrations are observed to remain constant, in a closed system, at a given temperature.

COMMUNICATION example 1

Write the equilibrium law expression for the reaction of nitrogen monoxide gas with oxygen gas to form nitrogen dioxide gas.

Solution

$$2\,NO(g) + O_2(g) \rightleftarrows 2\,NO_2(g)$$

$$K_c = \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]}$$

We use a balanced chemical equation with whole-number coefficients to write the mathematical expression of the equilibrium law. The coefficients of the balanced equation become the exponents of the amount concentrations. If the equation were to be written in reverse, the equilibrium law expression would simply be the reciprocal of the expression above, and the equilibrium constant would be the reciprocal of the one for the reaction as written here. Using the *products over reactants* convention results in a *relationship* between the numerical value of K_c and the forward extent of the equilibrium that is easier to visualize for the equation as written. The higher the numerical value of the equilibrium constant, the greater the tendency of the system to favour the forward direction; that is, the greater the equilibrium constant, the more the products are favoured at equilibrium.

COMMUNICATION example 2

The value of K_c for the formation of HI(g) from $H_2(g)$ and $I_2(g)$ is 40, at temperature t. Determine the value of K_c for the decomposition of HI(g) at the same temperature.

Solution

$$2\,HI(g) \rightleftarrows H_2(g) + I_2(g)$$

$$K_c = \frac{[H_2(g)][I_2(g)]}{[HI(g)]^2} = \frac{1}{40} = 0.025$$

Note that the decomposition reaction equation is the reverse of the formation reaction equation, and the value of K_c for decomposition is the reciprocal of the K_c for formation.

Experiments have shown that the value of the equilibrium constant depends on temperature. The value is also affected by very large changes in the equilibrium concentration of a reactant or a product. A moderate change in the concentration of any one of the reactants or products results in a change in the other concentrations, so that the equilibrium constant remains the same. The equilibrium constant provides only a measure of the equilibrium position of the reaction; it does not provide any information on the rate of the reaction. Because they hold for a significant range of different concentrations, equilibrium constant expressions have been found to be very useful, and K_c values for reactions are in common use throughout the scientific community.

Equilibrium constants are adjusted to reflect the fact that pure substances in solid or liquid (condensed) states have concentrations that are essentially fixed—the chemical amount (number of moles) per unit volume is a *constant* value. For example, a litre of liquid water at SATP has a mass of 1.00 kg (a chemical amount of 55.5 mol) and, thus, a fixed amount concentration of 55.5 mol/L. The concentration of condensed states is not included in a K_c expression—we assume that these constant values become part of the expressed equilibrium constant. Substances in a gaseous or dissolved state have *variable* concentrations, and must *always* be shown in an equilibrium law expression.

COMMUNICATION example 3

Write the equilibrium law expression for the decomposition of solid ammonium chloride to gaseous ammonia and gaseous hydrogen chloride.

Solution

$$NH_4Cl(s) \rightleftarrows NH_3(g) + HCl(g)$$

$$K_c = [NH_3(g)][HCl(g)]$$

The concentration of solid $NH_4Cl(s)$ is omitted from the equilibrium law expression.

The role of temperature in equilibrium constant expressions is critical, although the temperature is not written in the expression directly. The value of the equilibrium constant, K_c, always depends on the temperature. Any stated numerical value for an equilibrium constant, or any calculation using an equilibrium constant expression, *must* specify the reaction temperature at equilibrium.

Since equilibrium depends on the concentrations of reacting substances, these substances must be represented in the expression as they actually exist—meaning that ions in solution must be represented as individual entities. Equilibrium constant expressions are always written from the *net ionic* form of reaction equations, balanced with simplest whole-number (integral) coefficient values unless otherwise specified.

COMMUNICATION example 4

Write the equilibrium law expression for the reaction of zinc in copper(II) chloride solution.

Solution

$$Zn(s) + Cu^{2+}(aq) \rightleftarrows Cu(s) + Zn^{2+}(aq)$$

$$K_c = \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$$

Again, note that the solids, as well as the spectator ions (the chloride ions in this example), are omitted from the equilibrium law expression.

DID YOU KNOW?

Using Constant Relationships

You are already familiar with the usefulness of some other constant mathematical relationships about real phenomena. Finding a relationship that is constant for equilibrium concentrations is just another example.

If you examine circles of different sizes carefully, you discover that the distance around any circle divided by the distance across it (at the widest part) *always* gives the same (constant) answer, no matter how big or small the circle. This constant value, 3.14159…, is so useful that it has been given its own symbol, the Greek letter pi, π. This relationship is most usefully expressed as $C = \pi d$ because measuring a diameter is much easier than measuring a circumference.

Many other relationship expressions produce this same constant, including those usually used to calculate the area of a circle and the time period of a pendulum's swing.

EXTENSION

The Meaning of the Equilibrium Constant

Try this simulation to deepen your understanding of the equilibrium constant.

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LAB EXERCISE 15.B

Determining an Equilibrium Constant

Determining the equilibrium constant for a reaction at specific conditions is often essential for an industrial chemist. This knowledge is necessary before adjusting the reaction conditions in order to optimize production of the desired substances. Complete the Analysis of the investigation report.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	○ Evaluation
○ Hypothesis	○ Procedure	
○ Prediction	○ Evidence	

Purpose

The purpose of this investigation is to use the equilibrium law to determine the equilibrium constant at 200 °C for the decomposition reaction of the molecular compound phosphorus pentachloride.

Problem

What is the value of the equilibrium constant for the decomposition of phosphorus pentachloride gas to phosphorus trichloride gas and chlorine gas, at a temperature of 200 °C?

Evidence

equilibrium temperature = 200 °C
equilibrium concentrations:
$[PCl_3(g)] = [Cl_2(g)] = 0.014$ mol/L
$[PCl_5(g)] = 4.3 \times 10^{-4}$ mol/L

SUMMARY *Writing Equilibrium Law Expressions*

Write an equilibrium law expression based on a balanced equation for the reaction system. Use single whole-number coefficients, written in net ionic form, and ignore concentrations of pure solid or liquid phases:

If: $aA + bB \rightleftarrows cC + dD$

then: $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

An equilibrium constant value

- always depends on the system temperature
- is independent of the reagent concentrations
- is independent of any catalyst present
- is independent of the time taken to reach equilibrium
- is normally stated as a numerical value, ignoring any units
- is greater, the more the system favours the formation of products

Predicting Final Equilibrium Concentrations

For simple homogeneous systems, it is possible to algebraically predict reagent concentrations at equilibrium using a known value for K_c and initial reactant concentration values. For more complex systems, the calculation becomes more difficult—such systems are left for more advanced chemistry courses.

SAMPLE problem 15.2

In a 500 mL stainless steel reaction vessel at 900 °C, carbon monoxide and water vapour react to produce carbon dioxide and hydrogen. Evidence indicates that this reaction establishes an equilibrium with only partial conversion of reactants to products. Initially, 2.00 mol of each reactant is placed in the vessel. K_c for this reaction is 4.20 at 900 °C. What amount concentration of each substance will be present at equilibrium?

Write a balanced equation for the reaction equilibrium.

$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g) \qquad K_c = 4.20 \text{ at } 900\ °C$

Use the balanced equation to write the equilibrium law expression.

$$K_c = 4.20 = \frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]}$$

The *initial* amount concentrations of the CO(g) and the $H_2O(g)$ are the same:

$$c = \frac{2.00 \text{ mol}}{0.500 \text{ L}} = 4.00 \text{ mol/L} = [CO(g)] = [H_2O(g)]$$

An ICE table makes it easier to keep track of amount concentration changes that occur during a reaction, and to find the amount concentrations at equilibrium.

At equilibrium, let the final amount concentration of the product $H_2(g)$ be x mol/L (any convenient symbol could be used). Then $[CO_2(g)]$ must also be x mol/L, since the stoichiometric ratio of the reaction is 1:1:1:1. By this same reasoning, at equilibrium, the initial concentrations of CO(g) and $H_2O(g)$ must have *decreased* by x mol/L; so $[CO(g)] = [H_2O(g)] = (4.00 - x)$ mol/L. When you enter values for "Change" into the ICE table, you must show increases as "+", and decreases as "−".

Table 7 The $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$ Equilibrium

Concentration	$[CO(g)]$ (mol/L)	$[H_2O(g)]$ (mol/L)	$[CO_2(g)]$ (mol/L)	$[H_2(g)]$ (mol/L)
Initial	4.00	4.00	0	0
Change	$-x$	$-x$	$+x$	$+x$
Equilibrium	$(4.00 - x)$	$(4.00 - x)$	x	x

Substitute equilibrium concentrations in the equilibrium law expression.

$$4.20 = \frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]} = \frac{x^2}{(4.00 - x)^2}$$

Since the right side of the equation is a perfect square, solving for x is quite straightforward.

$$\sqrt{4.20} = \sqrt{\frac{x^2}{(4.00 - x)^2}}$$

$$2.05 = \frac{x}{4.00 - x}$$

$$x = (2.05)(4.00 - x)$$

$$= 8.20 - 2.05x$$

$$3.05x = 8.20$$

$$x = 2.69$$

Assign positive and negative signs and complete the ICE table.

Table 8 The $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$ Equilibrium

Concentration	$[CO(g)]$ (mol/L)	$[H_2O(g)]$ (mol/L)	$[CO_2(g)]$ (mol/L)	$[H_2(g)]$ (mol/L)
Initial	4.00	4.00	0	0
Change	−2.69	−2.69	+2.69	+2.69
Equilibrium	1.31	1.31	2.69	2.69

At equilibrium, at 900 °C, $[CO(g)] = [H_2O(g)] = 1.31$ mol/L and $[CO_2(g)] = [H_2(g)] = 2.69$ mol/L

Note that, if both initial reactant concentrations are not the same, solving the equation for x is more complicated, requiring use of the quadratic formula. Questions in this text are restricted to examples that do not require the quadratic formula for solution.

EXTENSION

Equilibrium Constant and Reaction Quotient

Is there any way of knowing whether or not a reaction is at equilibrium? If we know the concentrations of reactants and products, and the equilibrium constant at the appropriate temperature, we can use a concept called the "reaction quotient" to predict which way the reaction will proceed, or if it is already at equilibrium.

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WEB Activity

Simulation—Writing Equilibrium Expressions

This simulation allows you to select a reaction type and the initial reactant concentrations, which the program uses to plot the resulting equilibrium graph. You will then be guided through a series of questions.

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Section 15.1 Questions

1. Write a balanced equation with integer coefficients and the expression of the equilibrium law for each of the following reaction systems at fixed temperature.

(a) Hydrogen gas reacts with chlorine gas to produce hydrogen chloride gas in the industrial process that eventually produces hydrochloric acid.

(b) In the Haber process (Chapter 8), nitrogen reacts with hydrogen to produce ammonia gas.

(c) At some time in the future, industry and consumers may make more extensive use of the combustion of hydrogen as an energy source.

(d) When aqueous ammonia is added to an aqueous nickel(II) ion solution, the $Ni(NH_3)_6^{2+}(aq)$ complex ion is formed (**Figure 11**).

Figure 11
A $Ni^{2+}(aq)$ solution is green. Ammonia reacts with the nickel(II) ion to form the intensely blue hexaammine-nickel(II) ion, $Ni(NH_3)_6^{2+}(aq)$.

(e) In the Solvay process for making washing soda (Chapter 7), one reaction involves heating solid calcium carbonate (limestone) to produce solid calcium oxide (quicklime) and carbon dioxide.

(f) In Investigation 15.1, aqueous solutions of sodium sulfate and calcium chloride are mixed. (Remember to use a net ionic equation.)

(g) In a sealed can of soda, carbonic acid, $H_2CO_3(aq)$, decomposes to liquid water and carbon dioxide gas.

2. You can apply the empirical and theoretical concepts of equilibrium to many different chemical reaction systems. Use the generalizations from your study of organic chemistry to predict the position of equilibrium for bromine placed in a reaction container with ethylene at a high temperature.

3. Interpret the graph in **Figure 12** to answer the questions about the reaction. Hydrogen and iodine were placed in a reaction vessel, which was then sealed, and heated to 450 °C.

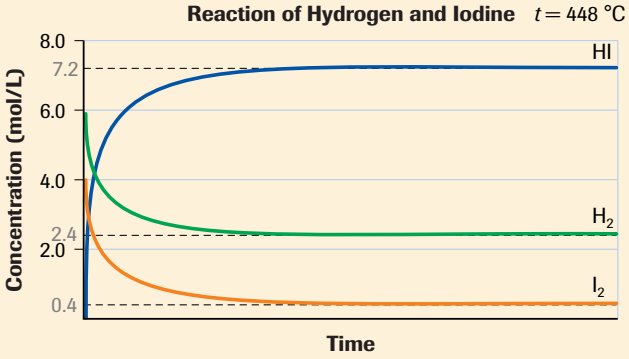

Figure 12
The progress of a hydrogen–iodine reaction

(a) All three substances are gases. If the container has a volume of 2.00 L, what chemical amount of each substance was present initially?

(b) What chemical amount of hydrogen iodide had formed at equilibrium? (Create an ICE table.)

(c) Describe the rate at which hydrogen is reacting from the moment the reactants are mixed to the time when equilibrium has been established, in terms of collision–reaction theory.

4. For each of the following, write the chemical reaction equation with appropriate equilibrium arrow, as shown in **Table 3** (page 680).

(a) The Haber process is used to manufacture ammonia fertilizer from hydrogen and nitrogen gases. Under less-than-desirable conditions, only an 11% yield of ammonia is obtained at equilibrium.

(b) A mixture of carbon monoxide and hydrogen, known as water gas, is used as a supplementary fuel in many large industries. At high temperatures, the reaction of coke and steam forms an equilibrium mixture in which the products (carbon monoxide and hydrogen gases) are favoured. (Assume that coke is pure carbon.)

(c) Because of the cost of silver, many high school science departments recover silver metal from waste solutions containing silver compounds or silver ions. A quantitative reaction of waste silver ion solutions with

copper metal results in the production of silver metal and copper(II) ions.

(d) One step in the industrial process used to manufacture sulfuric acid is the production of sulfur trioxide from sulfur dioxide and oxygen gases. Under certain conditions, the reaction produces a 65% yield of products.

5. Write the expression of the equilibrium law for the hydrogen–iodine–hydrogen iodide system at 448 °C. Using the evidence for System 1 as reported in **Table 1** on page 679, calculate the value of the equilibrium constant.

6. In the Haber process for synthesizing ammonia gas from nitrogen and hydrogen, the value of K_c is 6.0×10^{-2} for the reaction at 500 °C. In a sealed container at equilibrium at 500 °C, the concentrations of $H_2(g)$ and of $N_2(g)$ are measured to be 0.50 mol/L and 1.50 mol/L, respectively. Write the equilibrium law expression and calculate the equilibrium concentration of $NH_3(g)$.

7. At a certain constant (very high) temperature, 1.00 mol of HBr(g) is introduced into a 2.00 L container. Decomposition of this gas to hydrogen and bromine gases quickly establishes an equilibrium, at which point the amount concentration of HBr(g)is measured to be 0.100 mol/L.

(a) Write a balanced equation for the reaction.

(b) Write the equilibrium law expression.

(c) Calculate the chemical amount of HBr(g) present at equilibrium.

(d) Calculate the chemical amount of HBr(g) that has reacted to form $H_2(g)$ and $Br_2(g)$ products when equilibrium is established.

(e) Calculate the chemical amounts of $H_2(g)$ and $Br_2(g)$ that have been produced, and, thus, are present, when equilibrium is established.

(f) Calculate the amount concentration of all substances present at equilibrium.

(g) Calculate K_c for this reaction at this temperature.

8. To a heated reaction vessel with a volume of 1.00 L, a lab technician adds 6.23 mmol $H_2(g)$, 4.14 mmol of $I_2(g)$, and 22.40 mmol of HI(g). At equilibrium, a spectrophotometer is used to determine that the concentration of iodine vapour is 2.58 mmol/L. Construct an ICE table and find K_c for the reaction system

$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$.

9. Consider the system

$CO_2(g) + H_2(g) \rightleftarrows CO(g) + H_2O(g)$

Initially, 0.25 mol of water and 0.20 mol of carbon monoxide are placed in a 1.0 L reaction vessel. At equilibrium, spectroscopic evidence shows that 0.10 mol of carbon dioxide is present. Construct an ICE table and find K_c for this system.

10. Consider the system

$2\,HBr(g) \rightleftarrows H_2(g) + Br_2(g)$

Initially, 0.25 mol of hydrogen and 0.25 mol of bromine are placed into a 500 mL electrically heated reaction vessel. K_c for the reaction at the temperature used is 0.020.

(a) Find the concentrations of the substances at equilibrium.

(b) Calculate the chemical amount of each substance present at equilibrium.

11. Explain briefly how atomic theory, kinetic molecular theory, collision–reaction theory, and the concepts of reaction rate and reversible reactions are all necessary to explain chemical reaction equilibrium observations.

Extension

12. In a *very* long-term sense, Earth may be considered a closed system. One equilibrium of concern to scientists is the same one involved in carbonation of soft drinks, on a vastly larger scale. Scientists believe that over time, the carbon dioxide gas in the atmosphere should be in equilibrium with carbon dioxide dissolved in the oceans. They also know that the concentration of $CO_2(g)$ in the atmosphere has been increased significantly (by about 20%) in the last century, which, they believe, is mostly due to the burning of fossil fuels. Concerns about the consequences of global warming make it imperative that scientists improve their theories about the various cycles, processes, and equilibria involving this greenhouse gas. Research and summarize currently accepted theory about carbon dioxide dissolved in the oceans, and list some other cycles and systems involving reaction or production of $CO_2(g)$.

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15.2 Qualitative Change in Equilibrium Systems

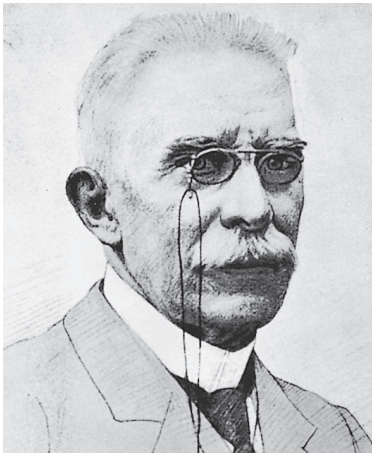

Figure 1
Henri Louis Le Châtelier (1850–1936), French chemist and engineer, worked in chemical industries. To maximize the yield of products, Le Châtelier used systematic trial and error. After measuring properties of equilibrium states in chemical systems, he discovered a pattern and stated it as a generalization. This generalization has been supported extensively by evidence and is now considered a scientific law. By convention, it is known as Le Châtelier's principle.

Observing the effects of varying system properties on the equilibrium of systems contributes greatly to our understanding of the equilibrium state. From a technological perspective, controlling the extent of equilibrium by manipulating properties is very desirable because control leads to more efficient and economic processes. From a scientific perspective, observing systems at equilibrium leads to improved theories that describe, explain, and predict the nature of equilibrium, thus increasing our understanding.

Equilibrium is an area of study where, historically, technology has led science. Reactions were first manipulated in response to some human need, although the reactions' responses were not explained until much later by successive theories of increasing validity. This section of the chapter will examine equilibrium manipulation in the same way, with empirical descriptions of equilibrium manipulation given first, followed by theoretical explanations of the observed results.

According to **Le Châtelier's principle**, when a chemical system at equilibrium is disturbed by a change in a property of the system, the system always appears to react in the direction that opposes the change, until a new equilibrium is reached (**Figures 1** to **3**). The application of Le Châtelier's principle involves a three-stage process: an initial equilibrium state, a shifting non-equilibrium state, and a new equilibrium state.

Le Châtelier's principle provides a method of predicting the response of a chemical system to an imposed change. Using this simple and completely empirical approach, chemical engineers could produce more of the desired products, making technological processes more efficient and more economical. For example, Fritz Haber used Le Châtelier's principle to devise a process for the economical production of ammonia from atmospheric nitrogen. (See the Haber process, Chapter 8, page 325.)

$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{2+}(aq)$

Figure 2
$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{2+}(aq)$
The test tube on the left is at equilibrium, as shown by the constant colour of the $FeSCN^{2+}(aq)$ ion. The equilibrium is disturbed by the addition of $Fe^{3+}(aq)$ ions. The system shifts and some of the additional $Fe^{3+}(aq)$ reacts to produce more $FeSCN^{2+}(aq)$, thus establishing a new equilibrium state. When the shift is complete, the concentration of $Fe^{3+}(aq)$ is higher than before (only some of the added ions react), the concentration of $SCN^{-}(aq)$ is lower, and the concentration of $FeSCN^{2+}(aq)$ is higher. The higher concentration of $FeSCN^{2+}(aq)$ is evident from the more intense colour of the solution observed in the test tube on the right.

INVESTIGATION 15.2 *Introduction*

Equilibrium Shifts (Demonstration)

In this investigation, you will be looking at two equilibrium systems:

$$N_2O_4(g) + \text{energy} \rightleftarrows 2\,NO_2(g)$$

colourless — reddish brown

$$CO_2(g) + H_2O(l) \rightleftarrows H^+(aq) + HCO_3^-(aq)$$

The second equilibrium system, produced by the reaction of carbon dioxide gas and water, is commonly found in the human body and in carbonated drinks. A diagnostic test is necessary to detect shifts in this equilibrium. Bromothymol blue, an acid–base indicator, can detect an increase or decrease in the hydrogen ion concentration in this system. Bromothymol blue turns blue when the hydrogen ion concentration decreases, and yellow when the hydrogen ion concentration increases.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

Purpose

The purpose of this demonstration is to test Le Châtelier's principle by studying two chemical equilibrium systems: the equilibrium between two oxides of nitrogen, and the equilibrium of carbon dioxide gas and carbonic acid.

Problem

How does a change in temperature affect the nitrogen dioxide–dinitrogen tetraoxide equilibrium system? How does a change in pressure affect the carbon dioxide–carbonic acid equilibrium system?

To perform this investigation, turn to page 700.

Le Châtelier's Principle and Concentration Changes

Le Châtelier's principle predicts that if the addition of a reactant to a system at equilibrium increases the concentration of that substance, then that system will undergo an **equilibrium shift** forward (to the right). The effect of the shift is that, temporarily, we observe the reactant concentration decreasing, as some of the added reactant changes to products. This period of change ends with the establishment of a *new* equilibrium state where, once again, there are no observable changes. The system has changed in such a way as to *oppose* the change introduced. For example, the production of freon-12, a CFC refrigerant, involves the following equilibrium reaction taking place at a fixed temperature:

$$CCl_4(l) + 2\,HF(g) \rightleftarrows CCl_2F_2(g) + 2\,HCl(g)$$

freon-12

To improve the yield of the primary product, freon-12, more hydrogen fluoride is added to the initial equilibrium system. The additional concentration of reactant disturbs the equilibrium state and the system shifts to the right, consuming some of the added hydrogen fluoride by reaction with carbon tetrachloride. As a result, more freon-12 is produced and a new equilibrium state is reached. In chemical reaction equilibrium shifts, an imposed concentration change is normally only *partially* counteracted, and the final equilibrium state concentrations of the reactants and products are usually different from the values at the original equilibrium state. See **Figure 3** for a graphic interpretation of the freon-12 equilibrium shift.

Note that adding more carbon tetrachloride, $CCl_4(l)$, would have no effect on the equilibrium state in the container. This reactant is (and stays) in liquid form, so its concentration is constant and would not be increased by increasing the amount of $CCl_4(l)$ present.

Adjusting an equilibrium state by adding and/or removing a substance is by far the most common application of Le Châtelier's principle. For industrial chemical reactions, engineers strive to design processes where reactants are added continuously and products are continuously removed, so that an equilibrium is never allowed to establish. If the reaction is always shifting forward, the process is always making product (and, presumably, the industry is always making money).

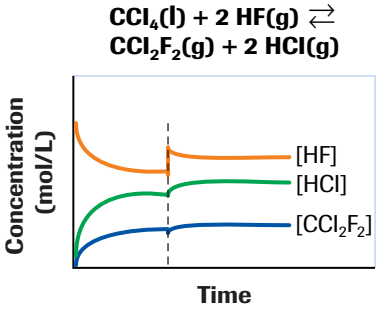

Figure 3

The reaction establishes an equilibrium that is disturbed (at the time indicated by the vertical dotted line) by the addition of HF(g). Some of the added HF reacts, decreasing in concentration, while the concentration of both products increases until a new equilibrium is established and concentrations become constant again. Note that the concentration of HF(g) at the new equilibrium is greater than at the original equilibrium, so the imposed change is only partly counteracted. The initial K_c value and final K_c value are the same.

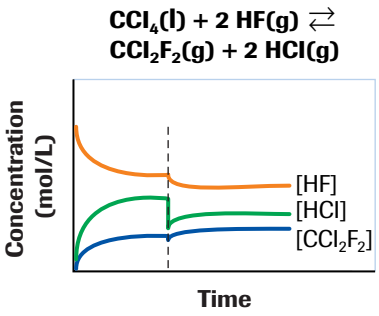

Figure 4
The reaction establishes an equilibrium that is disturbed (at the time indicated by the vertical dotted line) by the removal of HCl(g). The equilibrium shifts forward, increasing the concentration of both products while decreasing HF(g) concentration, until a new equilibrium is established. The initial K_c value and the final K_c value are the same.

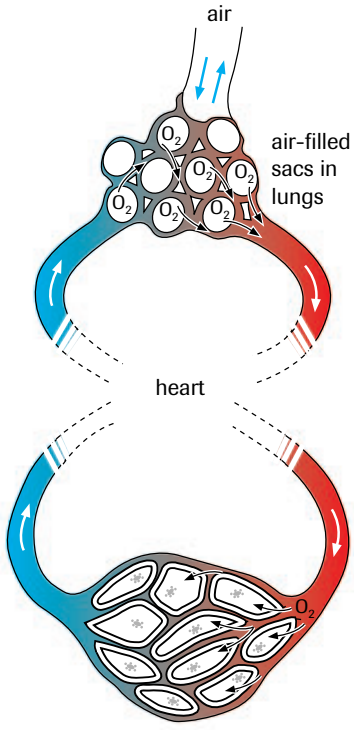

Figure 5
Oxygenated blood from the lungs is pumped by the heart to body tissues. The deoxygenated blood returns to the heart and is pumped to the lungs. Shifts in equilibrium occur over and over again as oxygen is picked up in the lungs and released throughout the body.

The removal of a product (if the removal decreases concentration as well as chemical amount) will also shift an equilibrium forward, producing more product to counteract the change imposed. The freon-12 reaction can be shifted forward by removing either gaseous product, since decreasing the amount of a gas lowers its concentration in any reaction container of fixed size (**Figure 4**).

The following equation represents the final step in the production of nitric acid:

$$3\ NO_2(g) + H_2O(l) \rightleftarrows 2\ HNO_3(aq) + NO(g)$$

In this industrial process, nitrogen monoxide gas is removed from the chemical system by a reaction with oxygen gas. The removal of the nitrogen monoxide causes the system to shift to the right—some nitrogen dioxide and water react, replacing some of the removed nitrogen monoxide. As the system shifts, more of the desired product, nitric acid, is produced.

Although equilibrium systems are important in industrial chemical production, they are even more vital in biological systems. A particularly important biological equilibrium is that of hemoglobin (a protein in red blood cells), oxygen, and oxygenated hemoglobin.

$$Hb + O_2 \rightleftarrows HbO_2$$

As blood circulates to the lungs, the high concentration of oxygen shifts the equilibrium to the right and the blood becomes oxygenated (**Figure 5**). As the blood circulates throughout the body, cell reactions consume oxygen. This removal of oxygen shifts the equilibrium to the left and more oxygen is released.

Collision–Reaction Theory and Concentration Changes

Collision–reaction theory provides a simple explanation of the equilibrium shift that occurs when a reactant concentration is increased. We assume that the number of reactant entities per unit volume suddenly increases, so that collisions are suddenly much more frequent for the forward reaction. The forward reaction rate, therefore, increases significantly. Since the reverse reaction rate is not changed, the opposing rates are no longer equal, and, for a time, the difference in rates results in an observed increase of products.

Of course, as the concentration of products increases, so does the reverse reaction rate. At the same time, the new forward rate decreases as reactant is consumed, until eventually the two rates become equal to each other again. The rates at the new equilibrium are faster than those at the original equilibrium, because the system now contains a larger number of particles (and, therefore, a higher concentration) in dynamic equilibrium. If a substance is removed, causing an equilibrium shift, the explanation is similar except that the initial effect is to suddenly decrease either the forward or the reverse rate by *decreasing* the concentration.

Addition or removal of a reagent present in pure solid or pure liquid state does not change the *concentration* of that substance. The reaction of condensed phases (solids and liquids) takes place only at an exposed surface—and if the surface area exposed is changed, it is always exactly the same change in available area for both forward and reverse reaction collisions. The forward and reverse rates change by exactly the same amount if they change at all, so equilibrium is not disturbed and no shift occurs.

Le Châtelier's Principle and Temperature Changes

The energy in a chemical equilibrium equation is treated as though it were a reactant or a product.

reactants + energy $\rightleftarrows$ products (endothermic in the forward direction)

reactants $\rightleftarrows$ products + energy (exothermic in the forward direction)

Heating or cooling a system adds or removes thermal energy from the system. In either situation, the equilibrium shifts to minimize the change. If the system is cooled, the equilibrium shifts so that more energy is produced. If the system is heated, the equilibrium shifts in the direction in which energy is absorbed.

For example, in the salt–sulfuric acid process used to produce hydrochloric acid, the system is heated in order to increase the percent yield of hydrogen chloride gas.

$$2\ NaCl(s) + H_2SO_4(l) + \text{energy} \rightleftarrows 2\ HCl(g) + Na_2SO_4(s)$$

Adding energy shifts the system to the right, absorbing some of the added energy.

In the production of sulfuric acid, the key reaction step is the equilibrium represented by the following equation. Percent yield of the product is increased at low temperature.

$$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g) + \text{energy}$$

Removing energy causes the system to shift to the right. This shift yields more sulfur trioxide while partially replacing the energy that was removed.

Collision–Reaction Theory and Energy Changes

Collision–reaction theory explains the equilibrium shift (that occurs when the thermal energy of a system at equilibrium is changed) as the result of an imbalance of reaction rates. Consider the previously mentioned reaction equation—a typical exothermic reaction. The reaction energy is shown this time in standard $\Delta_r H$ notation.

$$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g) \qquad \Delta_r H = -198\ kJ$$

We explain the result of cooling the system by assuming that *both* forward and reverse reaction rates are slower at lower temperatures, because the particles move more slowly and collide less frequently. The reverse rate decreases *more* than the forward rate, however. While the rates remain unequal, the observed result is the production of more product and the release of more heat energy. The shift causes concentration changes that will increase the reverse rate and decrease the forward rate until they become equal again, at a new, lower temperature (**Figure 6**).

Note that industrial exothermic equilibrium reactions are often carried out at high temperatures, even though adding heat energy shifts the equilibrium toward reactants (lowers the percent yield). The Haber process (Case Study, Section 8.3) is a good example. Energy is added because the forward and reverse reaction rates are too slow at lower temperatures to allow the reaction to reach equilibrium in a reasonable time. Making large quantities of the marketable product in a short time is much more important to a manufacturer than creating a small increase in the yield of each batch. Whenever possible, chemical engineers try to design a continuous process for an industrial reaction—one that shifts the reaction forward by constantly adding reactants, and constantly removing products. This system is no longer a closed system, so the reaction never establishes equilibrium. Such an industrial reaction may run continuously for months or even years.

BIOLOGY CONNECTION

CO_2 Transport

Many biological processes depend on equilibria. For example, the transportation of carbon dioxide depends on the $CO_2 \rightleftarrows H_2CO_3$ equilibrium system. In the tissues of the body where carbon dioxide is produced, the equilibrium shifts so that more carbonic acid is formed. In the lungs, the shift is in the reverse direction, as carbon dioxide is released. You will discover other examples of equilibria in a biology textbook.

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$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$

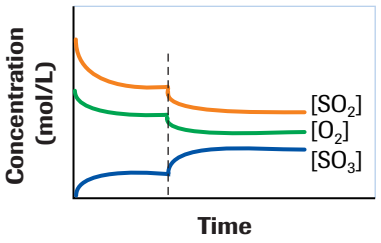

Figure 6
The reaction establishes an equilibrium that is disturbed (at the time indicated by the vertical dotted line) by a decrease in temperature. The equilibrium shifts forward, increasing the concentration of SO_3 product while decreasing the concentration of both reactants, until a new equilibrium is established. Because the temperature is changed, the final K_c value for this example is greater than the initial K_c value because the shift favours the forward reaction.

CAREER CONNECTION

Chemical Process Engineer

What role do chemical engineers play in designing systems and sequences of reactions for industrial chemical production? Research the education requirements, job prospects, and work assignments of people in this profession.

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Le Châtelier's Principle and Gas Volume Changes

According to Boyle's law, the pressure of a gas in a container is inversely proportional to the volume of the container. Since the amount concentration of a gas is directly proportional to its pressure, we can predict the possible effect of container volume change on the equilibrium position of homogeneous gaseous systems. Decreasing the volume by half doubles the concentration of every gas in the container. To predict whether a change in pressure will affect a system's equilibrium, you must consider the total chemical amount of gas reactants and the total chemical amount of gas products. For example, in the equilibrium reaction of sulfur dioxide and oxygen, three moles of gaseous reactants produce two moles of gaseous products.

$$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$$

If the volume is decreased, the overall pressure is increased. Increased pressure causes a shift to the right, which decreases the total number of gas molecules (three moles to two moles) and, thus, reduces the pressure. If the volume is increased, the pressure is decreased, and the shift is in the opposite direction. A system with equal numbers of gas molecules on each side of the equation, such as the equilibrium reaction between hydrogen and iodine (page 679), is not affected by a change in volume. Similarly, systems involving only liquids or solids are not affected by changes in pressure. Note that adding a gas that is not involved in the equilibrium (such as an inert gas) to the container will increase the overall pressure in the container, but will not cause a shift in equilibrium. Adding or removing gaseous substances not involved in the reaction does not change the concentrations of the reactant and product gases.

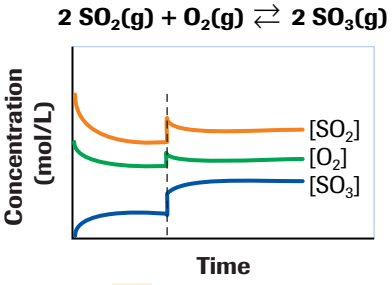

Figure 7
The reaction equilibrium is disturbed by a decrease in container volume (at the time indicated by the vertical dotted line). The equilibrium shifts forward, increasing the concentration of SO_3 while decreasing the concentration of reactants, until a new equilibrium is established. The initial K_c value and the final K_c value are the same.

Collision–Reaction Theory and Gas Volume Changes

When a system involving gaseous reactants and products is changed in volume, the resulting equilibrium shift is again explained as an imbalance of reaction rates.

$$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g) + 198\ kJ$$

Collision–reaction theory explains the result of decreasing the volume of this system by assuming that *both* forward and reverse reaction rates become faster because the concentrations of reactants and products both increase. For this example, however, the forward rate increases *more* than the reverse rate because there are more particles involved in the forward reaction. Consequently, the increase in the total number of collisions is greater for the forward reaction process. Again, while the rates remain unequal, the observed result is the production of more product. The shift causes concentration changes that gradually increase the reverse rate and decrease the forward rate until they become equal again (**Figure 7**).

Learning Tip

Since increasing the temperature of any exothermic reaction at equilibrium always shifts the equilibrium left (toward reactants), an increase in temperature must decrease the value of K_c for such a reaction. Similarly, increasing the temperature will increase the value of K_c for any endothermic reaction. You have already learned that the value of K_c is temperature dependent. No other change imposed on a system at equilibrium changes the numerical value of the equilibrium constant.

Catalysts and Equilibrium Systems

Catalysts are used in most industrial chemical systems. A catalyst decreases the time required to reach an equilibrium position, but does not affect the final position of equilibrium. The presence of a catalyst in a chemical reaction system lowers the activation energy for both forward and reverse reactions by an equal amount (Chapter 12), so the equilibrium establishes much more rapidly but at the same position as it would without the catalyst present. Forward and reverse rates increase equally. The final equilibrium concentrations are reached in a shorter time compared with the same, but uncatalyzed, reaction. The value of catalysts in industrial processes is to decrease the time required for equilibrium shifts created by manipulating other variables, allowing a more rapid overall production of the desired product.

SUMMARY Variables Affecting Chemical Equilibria

Variables	Imposed Change	Response of System
concentration	increase	shifts to consume some of the added reactant or product
	decrease	shifts to replace some of the removed reactant or product
temperature	increase	shifts to absorb some of the added energy
	decrease	shifts to replace some of the removed energy
volume (gaseous systems only)	increase (decrease in pressure)	shifts toward the side with the larger total chemical amount of gaseous entities
	decrease (increase in pressure)	shifts toward the side with the smaller total chemical amount of gaseous entities

Practice

1. What three types of changes shift the position of a chemical equilibrium?

2. For each of the following chemical systems at equilibrium, use Le Châtelier's principle to predict the effect of the change imposed on the chemical system. Indicate the direction in which the equilibrium is expected to shift. For each example, sketch the graph of concentrations versus time, plotted from just before the change to the established new equilibrium.

(a) $H_2O(l) + \text{energy} \rightleftarrows H_2O(g)$
The container is heated.

(b) $H_2O(l) \rightleftarrows H^+(aq) + OH^-(aq)$
A few crystals of NaOH(s) are added to the container.

(c) $CaCO_3(s) + \text{energy} \rightleftarrows CaO(s) + CO_2(g)$
$CO_2(g)$ is removed from the container.

(d) $CH_3COOH(aq) \rightleftarrows H^+(aq) + CH_3COO^-(aq)$
A few drops of pure $CH_3COOH(l)$ are added to the system.

3. Much methanol is produced industrially by the exothermic reaction $CO(g) + 2\,H_2(g) \rightleftarrows CH_3OH(l)$, carried out at high pressure (5–10 MPa) and temperature (250 °C) in the presence of several catalyst substances. Methanol is less flammable than gasoline, and so it is a safer fuel. It is the fuel used in open-wheel Champ Car racing, and also in the Indianapolis 500.

(a) State, in terms of forward and reverse reaction rates, why using a very high pressure of the reactant gases is economically desirable for the manufacturer .

(b) State in which direction a high temperature will shift this reaction equilibrium.

(c) Explain why using a high temperature is desirable, in terms of the time required for the reaction to reach equilibrium.

(d) Explain, in terms of equilibrium position and equilibrium shift, why this reaction is done in an open system, where reactants are continually added to the pressure vessel and liquid product is continually removed.

INVESTIGATION 15.3 *Introduction*

Testing Le Châtelier's Principle

The equilibria chosen for this investigation involve chemicals that provide coloured solutions. The investigation tests predictions about equilibrium shifts (made using Le Châtelier's principle) by observing colour changes.

In order to complete the Prediction section of the report, you must read the Design, Materials, and Procedure carefully. Then make a Prediction about the result of each change made in the Procedure.

Purpose

The purpose of this investigation is to test Le Châtelier's principle by applying stress to four different chemical equilibria.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

Problem

How does applying changes to conditions of particular chemical equilibria affect the systems?

Design

Stresses are applied to four chemical equilibrium systems and evidence is gathered to test predictions made using Le Châtelier's principle. Control samples are used in all cases.

To perform this investigation, turn to page 701.

Case Study

Urea Production in Alberta

Canada has a vast wealth of natural resources that we can use to produce many chemicals with an incredible variety of uses. Because plants require nitrogen for growth, the primary purpose of some of these chemicals is for agricultural use, such as nitrogen fertilizers. You have already learned that Alberta produces large amounts of ammonia, which can be used directly as a fertilizer. Ammonia is stored as a liquid at high pressure, and injected directly into the soil (see Section 8.3, Figure 7), but it is toxic and corrosive to human tissue, which makes it dangerous to use. Special equipment and care are required. Many food producers prefer to use a high-nitrogen, nontoxic, solid compound.

Urea (**Figure 8**) is another simple molecular chemical—also a nitrogen fertilizer—that is inexpensive, simple to produce, easy to transport, and extraordinarily useful. This chemical is used in the millions of tonnes, for applications as diverse as

- wastewater plants (for treating effluent)
- air transportation (for de-icing runways)
- forestry and agriculture (for fertilizer)
- livestock feeding (for a protein supplement)
- woodworking (for making glues and resins)
- construction supplies (for making insulation)
- furniture (for making particle board and chipboard)
- clothing (for making certain dyes)

Until the 1900s, the common source of this chemical was stale animal urine. The body forms this compound as its principal means of removing excess nitrogen. In fact, until the early 1800s, it was thought that this, or any other "organic" chemical extracted from living things, *always* had to be produced by a living organism. In 1828, however, Friedrich Wöhler, in a famous classic experiment, synthesized urea in his laboratory. His work forever changed the "organic" concept of chemistry. Early in the last century, an efficient industrial method was developed, and has since been used for mass production of this versatile and valuable substance.

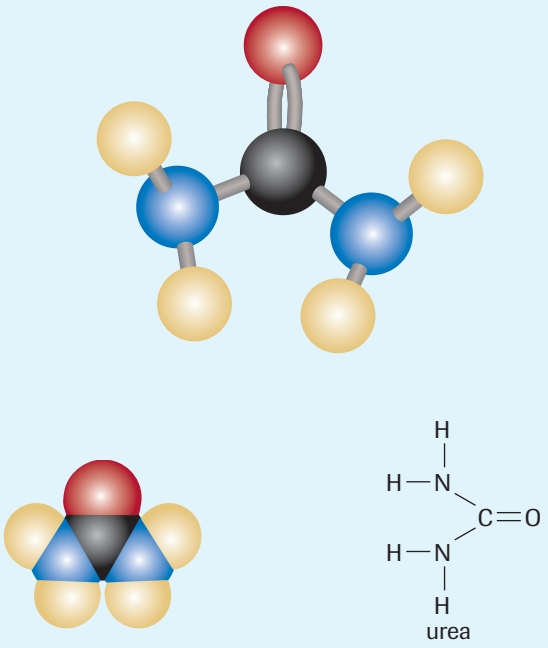

Figure 8
Urea is a small and simple molecule, but a critically important nitrogen-containing compound. It has a very high nitrogen percentage by mass, and is very soluble in water—both very important points for a compound to be useful as a plant fertilizer. Three different representations of the urea molecule are shown here.

Urea is produced through the reaction of ammonia, $NH_3(g)$, with carbon dioxide, $CO_2(g)$, at high temperature and

pressure. Most of the reactants exist in liquid form at the pressures used. A hot concentrated solution, containing about 80% urea by mass, results from this reaction. This hot solution is further concentrated and cooled through evaporation of the water content, to form either granules (angular crystals) or prills (small round pellets) of white solid urea (**Figure 9**). The overall reaction may be written as

$$CO_2(l) + 2\,NH_3(l) \rightleftarrows NH_2CONH_2(aq) + H_2O(l)$$
$$t = 150\text{–}200\ ^\circ C$$
$$P = 12\text{–}20\ MPa$$

The science and technology for urea production developed in response to a strong demand for this compound. The process depends on an understanding of reaction equilibrium, and of the effect (on equilibrium) of high temperature and pressure conditions. Also key was the design and construction of reaction containers (vessels) able to withstand high pressures and temperatures.

Sometimes, as well as building on existing scientific knowledge, new technology results in scientific advances. A technology, such as equipment to create very high pressures, may allow great leaps forward in science, such as the synthesis of completely new forms of crystalline solids. New observations then lead to new theories and sometimes even new laws.

Case Study Questions

1. There are two phase equilibria that shift during the reaction of carbon dioxide and ammonia. Write equilibrium equations to represent these phase changes, and use Le Châtelier's principle to explain how they are continuously being shifted, both by pressure, and also by the effect of the chemical reaction that is occurring in the vessel.
2. Crystallization of urea from aqueous solution can be expressed as a solubility equilibrium, according to the equation

   $$NH_2CONH_2(aq) \rightleftarrows NH_2CONH_2(s)$$

   (a) On which side of this equation would heat energy be written? Explain your reasoning.
   (b) Based on molecular structure and bonding theory, explain why you would expect urea to be a very highly soluble compound.
   (c) Urea granules that are bagged and sold for fertilizer use are quite uniform in size (**Figure 10**). Explain what physical process would likely be used to separate these granules from any larger or smaller granules that form during crystallization.

Figure 9
Prills form when sprayed droplets of very hot urea solution are made to fall through air in a huge tower, cooling and evaporating to dryness on the way down.

Figure 10
Urea fertilizer is a nitrogen source for crops.

Extension

3. Research Friedrich Wöhler's classic experiment of 1828. Write the balanced equation for the reaction he performed.

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4. Find out how much urea is produced annually in Alberta, where it is produced, and its current price per tonne. Assemble your findings into an attractive presentation.

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LAB EXERCISE 15.C

The Nitrogen Dioxide–Dinitrogen Tetraoxide Equilibrium

Complete the Prediction, Analysis, and Evaluation sections of the report.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (1, 2, 3)
○ Hypothesis	○ Procedure	
● Prediction	○ Evidence	

Purpose

The purpose of this problem is to use Le Châtelier's principle to predict the response of an equilibrium to an introduced change in conditions.

Problem

How does increasing the pressure affect the nitrogen dioxide–dinitrogen tetraoxide equilibrium?

Design

A sample of nitrogen dioxide gas is compressed in a syringe and the intensity of the colour is used as evidence to test the Prediction.

Evidence

The orange-brown nitrogen dioxide gas colour increases in intensity when the plunger on the syringe is depressed, and then decreases in intensity (**Figure 11**). The final colour is slightly more intense than the original colour (before moving the plunger).

Figure 11

$2\,NO_2(g) \rightleftarrows N_2O_4(g)$

An increase in pressure on the nitrogen dioxide–dinitrogen tetraoxide equilibrium in the closed system results initially in a more intense colour followed by a decrease in colour intensity.

INVESTIGATION 15.4 *Introduction*

Studying a Chemical Equilibrium System

Figure 2, page 690, shows the colours of aqueous solutions of iron(III), thiocyanate, and iron(III) thiocyanate ions. Use your knowledge of Le Châtelier's principle to write a Problem statement, and then design and carry out a simple investigation to determine whether the reaction as written is exothermic or endothermic.

Report Checklist

○ Purpose	● Design	● Analysis
● Problem	● Materials	● Evaluation (1, 2, 3)
○ Hypothesis	● Procedure	
● Prediction	● Evidence	

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{2+}(aq)$$

almost colourless + colourless ⇄ red

Purpose

The purpose of this investigation is to use Le Châtelier's principle to solve a problem concerning the effect of an energy change on the following equilibrium system.

To perform this investigation, turn to page 703.

WWW *WEB Activity*

Web Quest—Poison Afloat

Have you ever considered becoming a crime scene investigator? In this Web Quest, you are promoted to Chief Chem Crime Investigator. You are presented with a body and a series of clues… The detecting is up to you. You will have a chance to use your knowledge of chemistry to solve this puzzle and gather the evidence to unravel what happened.

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Section 15.2 Questions

1. The following equation represents part of the industrial production of nitric acid. Predict the direction of the equilibrium shift for each of the following changes. Explain any shift in terms of the changes in forward and reverse reaction rates.

$4\,NH_3(g) + 5\,O_2(g) \rightleftarrows 4\,NO(g) + 6\,H_2O(g) + \text{energy}$

(a) $O_2(g)$ is added to the system.
(b) The temperature of the system is increased.
(c) NO(g) is removed from the system.
(d) The pressure of the system is increased by decreasing the volume.

2. The following chemical equilibrium system is part of the Haber process for the production of ammonia.

$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g) + \text{energy}$

Suppose you are a chemical process engineer. Use Le Châtelier's principle to predict five specific changes that you might impose on the equilibrium system to increase the yield of ammonia.

3. In a solution of copper(II) chloride, the following equilibrium exists:

$CuCl_4^{2-}(aq) + 4\,H_2O(l) \rightleftarrows Cu(H_2O)_4^{2+}(aq) + 4\,Cl^-(aq)$

dark green — blue

For the following stresses put on the equilibrium, predict the shift in the equilibrium and draw a graph of concentration versus time to communicate the shift.
(a) Concentrated hydrochloric acid is added.
(b) Saturated aqueous silver nitrate is added, causing a precipitation reaction.

4. Identify the nature of the changes imposed on the following equilibrium system at the four times indicated by coordinates A, B, C, and D (**Figure 12**).

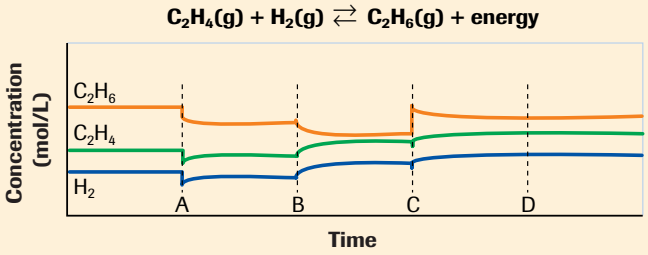

Figure 12
Graph showing four disturbances to an equilibrium system

5. In which of the following cases would an increase in temperature increase the percent yield at equilibrium?
(a) $H_2O(l) \rightleftarrows H_2O(g)$
(b) $N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g) \qquad \Delta_r H = -91\ kJ$
(c) $KOH(s) \rightleftarrows K^+(aq) + OH^-(aq) + \text{heat}$
(d) $2\,C(s) + 2\,H_2(g) \rightleftarrows C_2H_4(g) \qquad \Delta_r H = +53\ kJ$

6. Chloromethane (methyl chloride) is manufactured by "chlorinating" methane. For this reaction system at equilibrium, explain the effect of each of the imposed changes on the position of reaction equilibrium.

$CH_4(g) + Cl_2(g) \rightleftarrows CH_3Cl(g) + HCl(g) \qquad \Delta_r H$ is negative

(a) More methane is injected into the reaction vessel.
(b) The container volume is increased.
(c) The temperature is lowered.
(d) A catalyst is introduced into the system.

7. Ethyne (acetylene) is manufactured by a high-temperature combustion of methane, using a large excess of methane. For this endothermic reaction system at equilibrium, explain the effect of each of the imposed changes on the value of the equilibrium constant.

$6\,CH_4(g) + O_2(g) \rightleftarrows 2\,C_2H_2(g) + 10\,H_2(g) + 2\,CO(g)$

(a) More methane is injected into the reaction vessel.
(b) The container volume is decreased.
(c) The temperature is lowered.
(d) A catalyst is introduced into the system.

Extension

8. In a deep lake or in the ocean, the pressure that a human considers "normal" has doubled by the time a diver reaches a depth of 10 m, and increases by about one atmosphere for every extra 10 m, to a maximum of about 100 MPa at the deepest points in Earth's oceans. This fact is of major concern to scuba divers for several reasons. Pressure inside a scuba diver's lungs must constantly be adjusted to equal outside water pressure, otherwise the lungs could collapse upon diving, and could explode upon rising. In fact, the development of the pressure regulator (**Figure 13**) was the technology that made scuba diving possible.

The gases in a diver's lungs are dissolved to some extent in the blood that passes through. Pressure changes can change several solubility equilibria, with some serious effects. Research the gases dissolved in human blood, and what equilibrium shifts cause the diving conditions called nitrogen narcosis, and the "bends."

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Figure 13
The mouthpiece pressure from a diver's tank automatically adjusts for changes in depth.

INVESTIGATION 15.1

The Extent of a Chemical Reaction

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (1, 2, 3)
○ Hypothesis	● Procedure	
● Prediction	● Evidence	

In Chapter 8, you performed experiments that produced evidence that reactions are quantitative. In a quantitative reaction, the limiting reagent is completely consumed. To identify the limiting reagent, you can test the final reaction mixture for the presence of the original reactants. For example, in a diagnostic test, you might try to precipitate ions from the final reaction mixture that were present in the original reactants.

Purpose

The purpose of this investigation is to test the validity of the assumption that chemical reactions are quantitative.

Problem

What are the limiting and excess reagents in the chemical reaction of selected quantities of aqueous sodium sulfate and aqueous calcium chloride?

Design

Samples of sodium sulfate solution and calcium chloride solution are mixed in different proportions and the final mixture is filtered. Samples of the filtrate are tested for the presence of excess reagents, using the following diagnostic tests:

- If a few drops of $Ba(NO_3)_2(aq)$ are added to the filtrate and a precipitate forms, then sulfate ions are present.
  $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
- If a few drops of $Na_2CO_3(aq)$ are added to the filtrate and a precipitate forms, then calcium ions are present.
  $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

Materials

lab apron
eye protection
25 mL of 0.50 mol/L $CaCl_2(aq)$
25 mL of 0.50 mol/L $Na_2SO_4(aq)$
1.0 mol/L $Na_2CO_3(aq)$ in dropper bottle
saturated $Ba(NO_3)_2(aq)$ in dropper bottle
two 50 mL or 100 mL beakers
two small test tubes
10 mL or 25 mL graduated cylinder
filtration apparatus
filter paper
wash bottle
stirring rod

Soluble barium compounds are toxic. Remember to wash your hands before leaving the laboratory.

Barium nitrate in solid form is a strong oxidizing substance.

INVESTIGATION 15.2

Equilibrium Shifts (Demonstration)

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

In this investigation, you will be looking at two equilibrium systems:

$$\underset{\text{colourless}}{N_2O_4(g)} + \text{energy} \rightleftarrows \underset{\text{reddish brown}}{2\,NO_2(g)}$$

$$CO_2(g) + H_2O(l) \rightleftarrows H^+(aq) + HCO_3^-(aq)$$

The second equilibrium system, produced by the reaction of carbon dioxide gas and water, is commonly found in the human body and in carbonated drinks. A diagnostic test is necessary to detect some shifts in this equilibrium. Bromothymol blue, an acid–base indicator, can detect an increase or decrease in the hydrogen ion concentration in this system. Bromothymol blue turns blue when the hydrogen ion concentration decreases, and yellow when the hydrogen ion concentration increases.

Purpose

The purpose of this demonstration is to test Le Châtelier's principle by studying two chemical equilibrium systems: the equilibrium between two oxides of nitrogen, and the equilibrium of carbon dioxide gas and carbonic acid.

INVESTIGATION 15.2 *continued*

Problem

How does a change in temperature affect the nitrogen dioxide–dinitrogen tetraoxide equilibrium system? How does a change in pressure affect the carbon dioxide–carbonic acid equilibrium system?

Materials

lab apron
eye protection
two $NO_2(g)/N_2O_4(g)$ sealed flasks
carbon dioxide–hydrogen carbonate ion equilibrium mixture (pH = 7)
bromothymol blue indicator in dropper bottle
small syringe with needle removed (5 to 50 mL)
solid rubber stopper to seal end of syringe
beaker of ice–water mixture
beaker of hot water

Be careful with the flasks containing nitrogen dioxide: this gas is highly toxic. Use in a fume hood in case of breakage.

Procedure

1. Place the sealed $NO_2(g)/N_2O_4(g)$ flasks in hot and cold water baths (**Figure 1**) and record your observations.
2. Place two or three drops of bromothymol blue indicator in the carbon dioxide–hydrogen carbonate ion equilibrium mixture.
3. Draw some of the carbon dioxide–hydrogen carbonate ion equilibrium mixture into the syringe, and then block the end with a rubber stopper.
4. Slowly move the syringe plunger and record your observations.

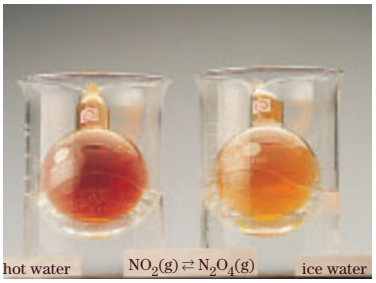

Figure 1
Each of these flasks contains an equilibrium mixture of dinitrogen tetraoxide and nitrogen dioxide. Shifts in equilibrium can be seen when one of the flasks is heated or cooled.

INVESTIGATION 15.3

Testing Le Châtelier's Principle

The equilibria chosen for this investigation involve chemicals that provide coloured solutions. This investigation tests predictions about equilibrium shifts (made using Le Châtelier's principle) by observing colour changes. For example, if the colour in Reaction 3 becomes more intensely red, the equilibrium has shifted right to produce more $FeSCN^{2+}(aq)$ ions, increasing their concentration. See **Table 1**.

In order to complete the Prediction section of the report, you must read the Design, Materials, and Procedure carefully. Then, make a Prediction about the result of each change made in the Procedure.

Purpose

The purpose of this investigation is to test Le Châtelier's principle by applying stress to four different chemical equilibria.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

Table 1 Solution Colours

Ion	Colour
$CoCl_4^{2-}(alc)$	blue
$Co(H_2O)_6^{2+}(alc)$	pink
$H_2Tb(aq)$	red
$HTb^-(aq)$	yellow
$Tb^{2-}(aq)$	blue
$Fe^{3+}(aq)$	pale yellow
$SCN^-(aq)$	colourless
$FeSCN^{2+}(aq)$	red
$Cu(H_2O)_4^{2+}(aq)$	pale blue
$Cu(NH_3)_4^{2+}(aq)$	deep blue

INVESTIGATION 15.3 *continued*

Problem

How does applying stresses to particular chemical equilibria affect the systems?

Part I

$$CoCl_4^{2-}(alc) + 6\ H_2O(alc) \rightleftarrows Co(H_2O)_6^{2+}(alc) + 4\ Cl^-(alc) + \text{energy}$$

Part II

$$H_2Tb(aq) \rightleftarrows H^+(aq) + HTb^-(aq)$$

$$HTb^-(aq) \rightleftarrows H^+(aq) + Tb^{2-}(aq)$$

Part III

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftarrows FeSCN^{2+}(aq)$$

Part IV

$$Cu(H_2O)_4^{2+}(aq) + 4\ NH_3(aq) \rightleftarrows Cu(NH_3)_4^{2+}(aq) + 4\ H_2O(l)$$

Design

Stresses are applied to four chemical equilibrium systems and evidence is gathered to test predictions made using Le Châtelier's principle. Control samples are used in all cases. For example, before adding sodium hydroxide to a new equilibrium solution, split the solution into two samples in order to have a control sample for colour comparison.

Part I Cobalt(II) Complexes

Water, saturated silver nitrate, and heat are added to, and heat is removed from, samples of the provided equilibrium mixture. Note: This reaction equilibrium is in solution using an alcohol solvent, shown as (alc), so the concentration of water is a variable in this system.

Part II Thymol Blue Indicator

Hydrochloric acid and sodium hydroxide are added to samples of the provided equilibrium mixture.

Part III Iron(III)–Thiocyanate Equilibrium

Iron(III) nitrate, potassium thiocyanate, and sodium hydroxide are added to samples of the provided equilibrium system.

Part IV Copper(II) Complexes

Aqueous ammonia and hydrochloric acid are added to samples of the provided equilibrium mixture.

Materials

lab apron
100 mL beaker
6 to 12 small test tubes
distilled water
eye protection
large waste beaker
test-tube rack
crushed ice
hot water bath
cobalt(II) chloride equilibrium mixture in ethanol
dropper bottles containing
- 0.2 mol/L $AgNO_3(aq)$
- thymol blue indicator
- 0.1 mol/L $HCl(aq)$
- 0.1 mol/L $NaOH(aq)$

iron(III) thiocyanate equilibrium mixture
- 0.2 mol/L $Fe(NO_3)_3(aq)$
- 0.2 mol/L $KSCN(aq)$
- 6.0 mol/L $NaOH(aq)$
- 0.1 mol/L $CuSO_4(aq)$
- 1.0 mol/L $NH_3(aq)$
- 1.0 mol/L $HCl(aq)$

The chemicals used may be corrosive or poisonous, and may cause other toxic effects. Exercise great care when using the chemicals and avoid skin and eye contact. Immediately rinse the skin if there is any contact. If any chemicals get in the eyes, flush eyes for a minimum of 15 min and inform the teacher. Ethanol is flammable. Make sure there are no open flames in the laboratory when using the ethanol solution of cobalt(II) chloride.

Procedure

Part I Cobalt(II) Complexes

1. Obtain 25 mL of the equilibrium mixture with the cobalt(II) chloride complex ions.
2. Place a small amount of the mixture into each of five small test tubes. Use the fifth test tube as a control for comparison purposes.
3. Add drops of water to one test tube until a change is evident. Record the evidence.
4. Add drops of 0.2 mol/L silver nitrate to another test tube and record the evidence.
5. Heat another equilibrium mixture in a hot water bath and record the evidence.
6. Cool an equilibrium mixture in an ice bath and record the evidence.

Part II Thymol Blue Indicator

7. Add about 5 mL of distilled water to each of two small test tubes.
8. Add 1 to 3 drops of thymol blue indicator to the water in each test tube to obtain a noticeable colour. Use one test tube of solution as a control.
9. Add drops of 0.1 mol/L $HCl(aq)$ to the experimental test tube to test for the predicted colour changes.
10. Add drops of 0.1 mol/L $NaOH(aq)$ to the same tube to test for the predicted colour changes.

INVESTIGATION 15.3 *continued*

Part III Iron(III)–Thiocyanate Equilibrium

11. Obtain about 20 mL of the iron(III)–thiocyanate equilibrium mixture.
12. Place about 5 mL of the equilibrium mixture in each of three test tubes. Use one test tube as a control.
13. Add drops of $Fe(NO_3)_3(aq)$ to one test tube until a change is evident.
14. Add drops of 6.0 mol/L NaOH(aq) to this new equilibrium mixture until a change occurs. (Iron(III) hydroxide has very low solubility.)
15. Add drops of KSCN(aq) to another equilibrium mixture until a change is evident.

Part IV Copper(II) Complexes

16. Obtain 2 mL of 0.1 mol/L $CuSO_4(aq)$ in a small test tube.
17. Add three drops of 1.0 mol/L $NH_3(aq)$ to establish the equilibrium mixture.
18. Add more 1.0 mol/L $NH_3(aq)$ to the above equilibrium mixture and record the results.
19. Add 1.0 mol/L HCl(aq) to the equilibrium mixture from step 18 and record the results.

Dispose of the chemicals as directed by your teacher. Identify each as toxic (to be collected) or nontoxic (disposable in the sink).

Ensure that all equipment and surfaces are clean and wash your hands thoroughly before leaving the laboratory.

INVESTIGATION 15.4

Studying a Chemical Equilibrium System

Figure 1 shows the colours of aqueous solutions of iron(III), thiocyanate, and iron(III) thiocyanate ions. Use your knowledge of Le Châtelier's principle to write a Problem statement, and then design and carry out a simple investigation to determine whether the reaction as written is exothermic or endothermic.

Report Checklist

○ Purpose	● Design	● Analysis
● Problem	● Materials	● Evaluation (1, 2, 3)
○ Hypothesis	● Procedure	
● Prediction	● Evidence	

Purpose

The purpose of this investigation is to use Le Châtelier's principle to solve a problem concerning the effect of an energy change on the following equilibrium system.

$$\underset{\text{almost colourless}}{Fe^{3+}(aq)} + \underset{\text{colourless}}{SCN^{-}(aq)} \rightleftarrows \underset{\text{red}}{FeSCN^{2+}(aq)}$$

Iron(III) compounds are irritants. Thiocyanate ion solutions are toxic. Avoid skin and eye contact. If there is any skin or eye contact, immediately rinse with plenty of water. Flush the eyes for at least 15 min and inform the teacher.

Figure 1
The iron–thiocyanate reaction

Chapter 15 SUMMARY

Outcomes

Knowledge

- define equilibrium and state the criteria that apply to a chemical system in equilibrium (15.1)
- identify, write, and interpret chemical equations for systems at equilibrium (15.1, 15.2)
- predict, qualitatively, using Le Châtelier's principle, shifts in equilibrium caused by changes in temperature, pressure, volume, concentration, or the addition of a catalyst, and describe how these changes affect the equilibrium constant (15.2)
- define K_c and write equilibrium law expressions for given chemical equations, using lowest whole-number coefficients (15.1)
- calculate equilibrium constants and concentrations for homogeneous systems when concentrations at equilibrium are known, when initial concentrations and one equilibrium concentration are known, and when the equilibrium constant and one equilibrium concentration are known (15.1)

STS

- state that the goal of science is knowledge about the natural world (15.1, 15.2)
- list the characteristics of empirical and theoretical knowledge (15.2)
- state that a goal of technology is to solve practical problems (15.2)

Skills

- initiating and planning: predict variables that can cause a shift in equilibrium (15.2); design an experiment to show equilibrium shifts (15.2); describe procedures for safe handling, storage, and disposal of materials used in the laboratory (15.1, 15.2)
- performing and recording: perform an experiment to test, qualitatively, predictions of equilibrium shifts (15.2)
- analyzing and interpreting: write the equilibrium law expression for a given equation (15.1); analyze, qualitatively, the changes in concentrations of reactants and products after an equilibrium shift (15.2); interpret data from a graph to determine when equilibrium is established, and determine the cause of a stress on the system (15.2)
- communication and teamwork: work collaboratively in addressing problems and communicate effectively (15.1, 15.2)

EXTENSION

CBC radio ONE QUIRKS & QUARKS

Plague and the Little Ice Age

A Dutch researcher discusses his theory that the atmospheric carbon dioxide equilibrium shifted when 40% of Europe's human population was killed by a plague in the 14th century. Could this have caused "the little ice age"?

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Key Terms

15.1

closed system
equilibrium
phase equilibrium
solubility equilibrium
chemical reaction equilibrium
dynamic equilibrium theory
forward reaction
reverse reaction
ICE table
equilibrium constant, K_c
equilibrium law

15.2

Le Châtelier's principle
equilibrium shift

Key Equations

For the reaction $a\,A + b\,B \rightleftarrows c\,C + d\,D$,

the equilibrium law is $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

MAKE a summary

1. Make a concept map, beginning with the word "Equilibrium" in the centre of a page. Link all of the Key Terms from this chapter, together with points of your own, to explain and illustrate how connections among these terms include the equilibrium law expression, ICE table format, Le Châtelier's principle, and points from the section Summaries.
2. Refer back to your answers to the Starting Points questions at the beginning of this chapter. How has your thinking changed?

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The following components are available on the Nelson Web site. Follow the links for *Nelson Chemistry Alberta 20–30*.

- an interactive Self Quiz for Chapter 15
- additional Diploma Exam-style Review questions
- Illustrated Glossary
- additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

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DO NOT WRITE IN THIS TEXTBOOK.

Part 1

1. A "closed" system for a chemical equilibrium means that
- A. the reaction container must be solid and sealed, with a fixed volume
- B. no substance involved in the equilibrium must be able to enter or leave
- C. pressure and temperature in the reaction vessel must be constant
- D. no chemical of any kind may be added to the reaction vessel

2. The possible equilibrium that is *not* dynamic is the one between
- A. the liquid and gas phases of octane
- B. chromate and dichromate ions in aqueous solution
- C. the downward force of gravity exerted by Earth on an object, and the upward force of a balance exerted on the object
- D. the oxygen dissolved in water in a lake and the oxygen dissolved in nitrogen in the atmosphere

3. NR In a reaction, 4.22 mol of product has formed but there are no more visible signs of change. Calculations show that as much as 6.00 mol of product could have formed from the chemical amounts of reactants used. The percent yield is _____ %.

Use this information to answer questions 4 to 6.

Sulfuric acid is the most common commercial acid, with millions of tonnes produced each year (**Figure 1**). The second step in the "contact" process for industrial production of sulfuric acid involves the oxidation of sulfur dioxide gas catalyzed by contact with $V_2O_5(s)$ powder. The reaction equation is

$$2\,SO_2(g) + O_2(g) \rightleftarrows 2\,SO_3(g) \qquad \Delta_r H^\circ = -198\ kJ$$

Figure 1
Most sulfuric acid is produced in plants such as this one by the contact process, which includes two exothermic combustion reactions. Sulfur reacts with oxygen, forming sulfur dioxide; then, sulfur dioxide, in contact with a catalyst, reacts with oxygen, forming sulfur trioxide. Sulfur trioxide and water form sulfuric acid.

4. Which is the correct form of the equilibrium law for this reaction, as the equation is written?

A. $K_c = \dfrac{[SO_2(g)]^2[O_2(g)]}{[SO_3(g)]}$

B. $K_c = [SO_2(g)]^2[O_2(g)][SO_3(g)]^2$

C. $K_c = \dfrac{[SO_2(g)]^2[O_2(g)]}{[SO_3(g)]^2}$

D. $K_c = \dfrac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$

5. The imposed condition that does *not* shift equilibrium toward the product is
- A. adding the vanadium pentoxide catalyst
- B. decreasing the temperature
- C. decreasing the container volume
- D. adding oxygen to the system container

6. If the equilibrium constant, K_c, for the above oxidation reaction at a given temperature is 2.4×10^3, then the constant for the reverse reaction (written as the decomposition of sulfur trioxide) is
- A. 2.4×10^3
- B. 4.2×10^{-4}
- C. 2.4×10^{-3}
- D. 4.2×10^4

7. If excess copper reacts in a solution of silver nitrate, it is correct to state that
   A. the reaction is not considered quantitative
   B. the equilibrium constant at SATP will have a numerical value between 1 and 100
   C. water is not written in the equilibrium law expression because it is a spectator species
   D. silver nitrate is not written in the equilibrium law expression because it is a species with a constant concentration

Use this information to answer questions 8 to 10.

Consider the following reaction to produce hydrogen, done as a first step in the industrial process to make ammonia. Methane (from natural gas) reacts with steam over a nickel powder catalyst. The reaction equation is

$$CH_4(g) + 2\,H_2O(g) + \text{heat energy} \rightleftarrows CO_2(g) + 4\,H_2(g)$$

8. This reaction is done in a laboratory autoclave (a stainless steel pressure vessel) and allowed to reach equilibrium. More methane is then injected into the autoclave. We can predict that, when a new equilibrium is reached (at the same temperature), the concentration of every reagent in the equation will have increased, *except* that of
   A. methane
   B. water
   C. carbon dioxide
   D. hydrogen

9. When this gaseous reaction system at equilibrium is disturbed by heating the autoclave, we theorize that
   A. both forward and reverse reaction rates increase, but the forward rate increases more
   B. the forward reaction rate does not change, but the reverse reaction rate increases
   C. the reverse reaction rate does not change, but the forward reaction rate increases
   D. both reaction rates increase equally, so the equilibrium position is unchanged

10. NR A test reaction is done starting with only methane and excess water in the autoclave. If the initial concentration of methane is 0.110 mol/L, and the methane concentration at equilibrium is 0.010 mol/L, then the equilibrium concentration of hydrogen is _____ mol/L.

Part 2

11. **Define** chemical equilibrium empirically.

12. What main idea explains chemical equilibrium?

13. What phrase is used to **describe** a reaction equilibrium in which the proportion of reactants to products is quite high?

14. **Describe** and **explain** a situation in which a carbonated soft drink is in
   (a) a non-equilibrium state
   (b) an equilibrium state

15. **Predict** whether adding a catalyst affects a state of equilibrium. What does the catalyst do?

16. For each of the following descriptions, write a chemical equation for the system at equilibrium. Communicate the position of the equilibrium with equilibrium arrows. Then write a mathematical expression of the equilibrium law for each chemical system.
   (a) A combination of low pressure and high temperature provides a percent yield of less than 10% for the formation of ammonia in the Haber process.
   (b) At high temperatures, the formation of water vapour from hydrogen and oxygen is quantitative.
   (c) The reaction of carbon monoxide with water vapour to produce carbon dioxide and hydrogen has a percent yield of 67% at 500 °C.

17. Scientists and technologists are particularly interested in the use of hydrogen as a fuel. **Interpret** this reaction equation by predicting the relative proportions of reactants and products in this system at equilibrium.

$$2\,H_2(g) + O_2(g) \rightleftarrows 2\,H_2O(g) \quad K_c = 1 \times 10^{80} \text{ at SATP}$$

Use this information to answer questions 18 to 24.

The solubility of pure oxygen in contact with liquid water at SATP is very low: only about 42 ppm, or 42 mg/L. The solubility equilibrium when water is in contact with air (21% oxygen) at SATP, is even lower: about 8.7 mg/L. The equilibrium equation is

$$O_2(g) \rightleftarrows O_2(aq)$$

18. Write the equilibrium law expression for a saturated solution of oxygen in water.

19. If the gas in the closed system is pure oxygen, the solubility is higher than it is if the gas is air. Express the solubility of pure oxygen in water at SATP as an amount concentration.

20. Express the concentration of pure oxygen gas at SATP as an amount concentration. (Recall that the molar volume of gases at SATP is 24.8 L/mol.)

21. Use the answers to the previous two questions to **determine** the value of K_c for an equilibrium of pure oxygen gas in contact with its saturated solution at SATP.

22. **Predict** whether the value of K_c for this equilibrium will be different for an equilibrium of air in contact with water at 25 °C. **Predict** which system condition changes will, and which will not, change the value of an equilibrium constant.

23. In terms of the equilibrium law, **explain** why more oxygen dissolves in water when the gas above it is pure oxygen than when the gas above it is air.

24. The quality of surface water in lakes and streams (**Figure 2**) is of critical importance to society. Dissolved oxygen content of the surface fresh water in Canada averages 10 ppm. **Explain** what stress is placed upon fish and other organisms in streams, lakes, and wetlands if climate change increases the average temperature of the water.

Figure 2
The Bow River begins as a cold, glacier-fed mountain stream with a higher-than-average oxygen content, and is world famous for its trout fly fishery. It also supplies the city of Calgary with water for a million people daily, as well as providing water for agriculture in southern Alberta.

25. In many processes in industry, engineers try to maximize the yield of a product. **Outline** how concentration can be manipulated in order to increase the yield of a product.

26. DE In a container at high temperature, ethyne (acetylene) and hydrogen react to produce ethene (ethylene). No ethene is initially present.

$$C_2H_2(g) + H_2(g) \rightleftarrows C_2H_4(g)$$

The initial concentrations of both acetylene and hydrogen are 1.00 mol/L. Later, at equilibrium, the concentration of ethene is 0.060 mol/L.

(a) Use an ICE table to **determine** the equilibrium constant.

(b) **Sketch** a reaction progress graph to show the change in concentration values over time, from the beginning of the reaction to equilibrium.

27. $H_2(g) + Br_2(g) \rightleftarrows 2\,HBr(g) \quad K_c = 12.0$ at t °C

DE (a) 8.00 mol of hydrogen and 8.00 mol of bromine are added to a 2.00 L reaction container. Construct an ICE table and use it to **predict** the concentrations at equilibrium.

(b) 12.0 mol of hydrogen and 12.0 mol of bromine are added to a 2.00 L reaction container. Construct an ICE table and use it to **predict** the concentrations at equilibrium.

28. $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g) \quad K_c = 4.00$ at 900 °C

In a container, carbon monoxide and water vapour react to produce carbon dioxide and hydrogen. The equilibrium concentrations are $[H_2O(g)] = 2.00$ mol/L, $[CO_2(g)] = 4.00$ mol/L, and $[H_2(g)] = 2.00$ mol/L.
Determine the equilibrium concentration of carbon monoxide.

29. Write a statement of Le Châtelier's principle.

30. What variables are commonly manipulated to shift a chemical equilibrium system?

31. **Describe** how a change in volume of a closed system containing a gaseous reaction at equilibrium affects the pressure of the system.

32. DE In a sealed container, nitrogen dioxide is in equilibrium with dinitrogen tetraoxide.

$$2\,NO_2(g) \rightleftarrows N_2O_4(g) \quad K_c = 1.15,\ t = 55\ °C$$

(a) Write the mathematical expression for the equilibrium law applied to this chemical system.

(b) If the equilibrium concentration of nitrogen dioxide is 0.050 mol/L, **predict** the concentration of dinitrogen tetraoxide.

(c) **Predict** the shift in equilibrium that will occur when the concentration of nitrogen dioxide is increased.

33. **Predict** the shift in the following equilibrium system resulting from each of the following changes:

$$4\,HCl(g) + O_2(g) \rightleftarrows 2\,H_2O(g) + 2\,Cl_2(g) + 113\ kJ$$

(a) an increase in the temperature of the system

(b) a decrease in the system's total pressure due to an increase in the volume of the container

(c) an increase in the concentration of oxygen

(d) the addition of a catalyst

34. Chemical engineers use Le Châtelier's principle to predict shifts in chemical systems at equilibrium resulting from changes in the reaction conditions. **Predict** the changes necessary to maximize the yield of product in each of the following industrial chemical systems:

(a) the production of ethene (ethylene)
$C_2H_6(g) + \text{energy} \rightleftarrows C_2H_4(g) + H_2(g)$

(b) the production of methanol
$CO(g) + 2\,H_2(g) \rightleftarrows CH_3OH(g) + \text{energy}$

35. Apply Le Châtelier's principle to **predict** whether, and in which direction, the following established equilibrium would be shifted by the change imposed:

$2\,CO(g) + O_2(g) \rightleftarrows 2\,CO_2(g)$ + heat energy

(a) temperature is increased
(b) vessel volume is increased
(c) oxygen is added
(d) platinum catalyst is added
(e) carbon dioxide is removed

36. For each example, **predict** whether, and in which direction, an established equilibrium would be shifted by the change imposed. **Explain** any shift in terms of changes in forward and reverse reaction rates.

(a) $Cu^{2+}(aq) + 4\,NH_3(g) \rightleftarrows Cu(NH_3)_4{}^{2+}(aq)$
$CuSO_4(s)$ is added
(b) $CaCO_3(s)$ + energy $\rightleftarrows CaO(s) + CO_2(g)$
temperature is decreased
(c) $Na_2CO_3(s)$ + energy $\rightleftarrows Na_2O(s) + CO_2(g)$
sodium carbonate is added
(d) $H_2CO_3(aq)$ + energy $\rightleftarrows CO_2(g) + H_2O(l)$
vessel volume is decreased
(e) $KCl(s) \rightleftarrows K^+(aq) + Cl^-(aq)$
$AgNO_3(s)$ is added
(f) $CO_2(g) + NO(g) \rightleftarrows CO(g) + NO_2(g)$
vessel volume is increased
(g) $Fe^{3+}(aq) + SCN^-(aq) \rightleftarrows FeSCN^{2+}(aq)$
$Fe(NO_3)_3(s)$ is added

37. **Predict** in which of the following equilibria a decrease in temperature favours the forward reaction.

(a) $Br_2(l) \rightleftarrows Br_2(g)$
(b) $N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$ $\Delta_r H$ is negative
(c) $LiCl(s) \rightleftarrows Li^+(aq) + Cl^-(aq)$ + heat
(d) $6\,C(s) + 3\,H_2(g) \rightleftarrows C_6H_6(l)$ $\Delta_r H = +49$ kJ
(e) $CaCO_3(s)$ + energy $\rightleftarrows CaO(s) + CO_2(g)$

Use this information to answer questions 38 and 42.

Alberta's petroleum industry has a chronic problem—all fossil fuels found in the province contain some sulfur. If not removed, this sulfur will react upon burning to release $SO_2(g)$. Sulfur dioxide is very irritating to lung tissue and is highly corrosive; thus, it is a major contributor to air pollution, acid rain, and respiratory disease. Furthermore, sulfur impurities may damage the fuel injection and anti-pollution systems of modern internal combustion engines if not removed from gasoline and diesel fuels. For these reasons, recent Canadian legislation requires that sulfur content in diesel fuels sold for on-road use must be less than 15 ppm (15 mg/kg) by July, 2006.

In a refinery or bitumen upgrader, the sulfur is first removed from fossil fuel feedstock by cracking and/or hydrogenation, resulting in reaction of the sulfur to produce (*extremely* toxic) $H_2S(g)$. Standard industry technology to remove hydrogen sulfide gas from petrochemical gas stream mixtures involves the use of an amine scrubber unit, in a two-step process that depends on two kinds of equilibrium. For simplicity, assume that an amine scrubber reaction vessel contains a 25% aqueous solution of diethanolamine $(C_2H_4OH)_2NH(aq)$, which approximates the actual solution used in the various oil sands plants in Alberta.

38. DE The scrubbing operation involves a gas mixture of low-molar-mass hydrocarbons, carbon dioxide, and hydrogen sulfide. This mixture of gases is injected into the scrubber unit at high pressure, with the scrubber solution at about 40 °C. For hydrogen sulfide, first the toxic gas dissolves

$H_2S(g) \rightleftarrows H_2S(aq)$ (negative $\Delta_r H$)

which is followed immediately by the chemical reaction

$(C_2H_4OH)_2NH(aq) + H_2S(aq) \rightleftarrows (C_2H_4OH)_2NH_2{}^+(aq) + HS^-(aq)$ (negative $\Delta_r H$)

(a) Draw a structural formula for diethanolamine.
(b) **Explain**, using Le Châtelier's principle, how the relatively low temperature and high pressure act to help the scrubber solution "absorb" toxic hydrogen sulfide.

39. When the unabsorbed hydrocarbon gases are removed from the scrubber unit, the sulfur atoms remain behind, trapped in solution as hydrogen sulfide ions. In the next process step, the scrubber solution is "regenerated": the absorbed toxic compound is now emitted from solution and removed from the reaction vessel. Use Le Châtelier's principle to **describe** how conditions should be altered in the scrubber vessel, to shift equilibrium positions to make this process as efficient as possible.

40. When carbon dioxide gas "dissolves" in water, the process is more correctly thought of as being an exothermic chemical reaction *with* water, to form aqueous carbonic acid. Soft drink beverages are "carbonated" in this way, at high pressure. Write and balance an equilibrium equation for this reaction.

41. Carbonic acid, $H_2CO_3(aq)$, reacts exothermically with basic aqueous diethanolamine in essentially the same way that hydrosulfuric acid, $H_2S(aq)$, does in question 38. Write and balance the equilibrium equation for this reaction, and use it to **explain** whether the process conditions for scrubbing $H_2S(g)$ should work to remove $CO_2(g)$ as well.

Extension

42. DE Work cooperatively to research, assemble, and present a more complete and accurate summary of the operation of a typical Alberta industrial amine "scrubber" system. Your presentation should include

- a description of the role of chemical equilibrium in the system
- information on applications of this process throughout Alberta
- the use of the best features of any available word processing or slideshow software

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43. A halogen light bulb contains a tungsten (wolfram) filament, W(s), in a mixed atmosphere of a noble gas and a halogen; for example, Ar(g) and $I_2(g)$ (**Figure 3**). The operation of a halogen lamp depends, in part, on the equilibrium system

$$W(s) + I_2(g) \rightleftarrows WI_2(g)$$

Figure 3
Halogen light bulbs are more efficient than ordinary incandescent bulbs, but they burn so hot they may require special fixtures, and must be treated with extra care.

Research and **describe** the role of temperature in the operation of a halogen lamp. For example, **how** is it possible for a halogen lamp to operate with the filament at 2700 °C when the tungsten normally would not last very long at this high temperature? **Why** is such a high temperature desirable?

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44. DE When the Olympic Games were held in Mexico in 1968, many athletes arrived early to train in the higher altitude (2.3 km) and lower atmospheric pressure of Mexico City. Exertion at high altitudes, for people who are not acclimatized, may make them dizzy or "lightheaded" from lack of oxygen. **Explain** this observation. Your explanation should include

- the theory of dynamic equilibrium
- Le Châtelier's principle
- a description of how people who normally live at high altitudes are physiologically adapted to their reduced-pressure environment

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